

Preparation of chemically modified *Macadamia* nutshells for adsorptive removal of selected heavy metals

by

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree Magister Technologiae to the Department of Chemistry, Vaal University of Technology, Vanderbijlpark.

It has not been submitted before for any degree or examination to any other University.



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16th Day of Oct 2017

Abstract

The abundance of agricultural waste materials has led to its use as adsorbents for trace metal adsorption. The raw *Macadamia* nutshell (RMN) powder was treated with a hydrochloric acid solution to obtain acid modified *Macadamia* nutshells (AMM), and with sodium hydroxide solution to obtain base modified *Macadamia* nutshells (BMM). Then, the AMM and BMM materials were grafted with 0.5 M, 1 M, and 2 M acrylic acid. The different AMM grafted materials were labelled 0.5 GAM, 1 GAM and 2 GAM representing the different grafting ratios. The same naming order was followed for the BMM grafted materials, that is, 0.5 GBM, 1 GBM and 2 GBM corresponding to different concentrations used.

The prepared *Macadamia* based adsorbents were characterized using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), carbon, hydrogen, nitrogen and sulphur (CHNS) analysis, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis. The determination of surface properties such as the point of zero charge (pH_{PZC}), bulk density and the surface negative charge was accomplished with appropriate wet chemistry methods. The adsorption of selected trace metals (Cu(II), Cd(II), Co(II), and Cr(VI)) was done in batch experiments. Atomic absorption spectroscopy (AAS) was used for the determination of metal ions concentrations and total Cr. The ultraviolet-visible (UV-Vis) spectroscopy was used for the determination of Cr(VI) concentration remaining in solution after adsorption.

The RMN, AMM, and BMM adsorbents showed potential in removing more than 45% Cu(II) ions, but less than 30% for both Cd(II) and Co(II) ions. However, more

than 90% removal of Cr(VI) ions was achieved with the same adsorbents. Consequently, only the adsorption of Cr(VI) was further investigated in the study due to the higher removal efficiency displayed by the *Macadamia* based biosorbents. The optimum adsorption conditions for the RMN, AMM, and BMM materials were found to be pH 2, 100 mg/L initial concentration of Cr(VI), 600 min contact time and 0.2 g adsorbent mass. The ideal conditions for the 0.5 GAM and 0.5 GBM were found to be pH 2, 25 mg/L initial concentration of Cr(VI), 180 min contact time, and 0.15 g adsorbent mass. The optimum temperature was found to be 40°C for all materials. A volume of 20 mL was used for all batch experiments. The RMN, AMM, BMM, 0.5 GBM, and 0.5 GAM adsorption mechanisms were better described by the Langmuir isotherm which predicted a monolayer sorption process. The kinetic data fitted better to the pseudo second-order rate model which signified a chemisorption type of interaction. The thermodynamic parameters showed that the adsorption reaction was feasible, spontaneous and endothermic. The *Macadamia* based materials showed greater potential as adsorbents for the adsorption of Cr(VI) ions from aqueous solution compared to the other selected trace metal ions [Cd(II), Cu(II) and Co(II)].

Dedications

To the Ntuli and Zulu family and everyone who has a dream of becoming an academic researcher.

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Abbreviations and acronyms

FTIR	Fourier transform infrared
TGA	Thermo-gravimetric analysis
SEM	Scanning electron microscopy
BET	Brunauer, Emmett and Teller
PXRD	Powder X-ray diffraction
CHNS	Carbon, hydrogen, nitrogen and sulfur
PZC	Point of zero charge
AAS	Atomic absorption spectroscopy
UV-Vis	Ultraviolet-visible
RMN	Raw <i>Macadamia</i> nutshells
AMM	Acid-modified <i>Macadamia</i> nutshells
BMM	Base-modified <i>Macadamia</i> nutshells
0.5 GAM	0.5 M grafted acid modified <i>Macadamia</i> nutshells

1 GAM	1 M grafted acid modified <i>Macadamia</i> nutshells
2 GAM	2 M grafted acid modified <i>Macadamia</i> nutshells
0.5 GBM	0.5 M grafted base modified <i>Macadamia</i> nutshells
1 GBM	1 M grafted base modified <i>Macadamia</i> nutshells
2 GBM	2 M grafted base modified <i>Macadamia</i> nutshells
XPS	X-Ray photoelectron spectroscopy

Layout of dissertation

Chapter 1 is a brief overview of the research study which consists of the introduction, purpose of the study and the justification as to why the study was undertaken. Chapter 2 deals with the literature review on the selected trace metals Cd(II), Co(II), Cu(II), and Cr(VI), alongside the different methods that have been used to remove these trace metals from aqueous solutions. The advantages and disadvantages of the described methods of removal have been deliberated with additional focus placed on adsorption particularly by means of chemically treated and untreated agricultural waste adsorbents. Towards the culmination of this chapter a discussion on the parameters that influence adsorption and desorption or adsorbent regeneration are articulated. The aim and objectives of this study are outlined in Chapter 3, together with research questions, hypothesis, and the research contributions.

Chapter 4 provides the details of the chemicals and equipment used in this study. Experimental procedures such as the modification of the adsorbent with different chemical methods and the various wet chemistry methods that were used for the characterization of the adsorbent are also outlined in this chapter. At the end of this chapter, the adsorption and desorption experiments are described.

Chapter 5 deliberates on the results and discussion generated from different experiments conducted. This chapter is subdivided into three sections the adsorbents characterization (section 5.1) and the results from the adsorption and desorption experiments (section 5.2). The adsorption isotherms, kinetic models, and thermodynamic models are discussed in section 5.3. The conclusions and recommendations drawn from the results are summarized in Chapter 6.

Chapter One

1.1 Introduction

Planet earth consists of enormous quantities of water but merely less than 3% is freshwater, the rest remains saline water. Therefore, appropriate administration and dissemination of freshwater intended for approximately six billion people as well as the numerous additional natural life forms on planet earth is of paramount importance (UN WWAP, 2003). Toxic trace metal ions waste contributes towards freshwater contamination through industrial practices and inconsiderate discarding of trace metal containing waste to underground and surface water (Garcia-Reyes and Rangel-Mendez, 2010). Examples of trace metals found in aquatic streams include chromium (Cr), cadmium (Cd), copper (Cu), and cobalt (Co). Industries that contribute towards water pollution by trace metal ions includes clothing (Rovira *et al.*, 2015), mining (Castro-larragoitia *et al.*, 1997), electroplating (Legg *et al.*, 1996), steel (Hashemi, Shokri and Tahvildari, 2016), alloy production (Melchers, 2007), agricultural (Xiao-nan *et al.*, 2015), pharmaceutical (Sirés and Brillas, 2012), paint (Turner, 2010), and pulp and paper industries (Suthar *et al.*, 2014).

Trace metal ions remain toxic towards all life arrangements due to their non-biodegradable and persistence nature (Namasivayam and Ranganathan, 1995). At certain concentration levels, trace metal ions are capable of causing human health problems such as epigastric pain, nausea, vomiting and severe diarrhea (Selomulya *et al.*, 1999), and brain impairment (Akar *et al.*, 2009). The requirement to remove high levels of trace metal ions from aquatic streams is a matter of great importance

and must be attended to immediately for the preservation of all life forms (Kushwaha *et al.*, 2012).

Methods such as filtration (Al-rashdi *et al.*, 2013), magnetic separation (Rikers *et al.*, 1998), reverse osmosis (Redondo and Lomax, 2001), membrane technology (Yoon *et al.*, 2009), ion-exchange (Gode and Pehlivan, 2005), lime neutralization (González *et al.*, 2011) and solvent extraction (Wassie and Srivastava, 2016), have been used for the removal of trace metals from various matrices. The aforementioned methods suffer from drawbacks such as inadequate metal ion removal, generation of noxious sludge, high cost and substantial consumption of energy (Abdolali *et al.*, 2014).

Biomaterials derived from agricultural waste have received much attention by researchers seeking to develop low-cost and efficient materials for adsorption of pollutants (Miretzky and Cirelli, 2010; Gupta *et al.*, 2015). Biomaterials have been used for the removal of various pollutants (Gupta *et al.*, 2015) including dyes (Mittal *et al.*, 2010; Dawood and Sen, 2012), lead (Pholosi *et al.*, 2013), zinc (Paduraru *et al.*, 2015), and cadmium (Cheraghi *et al.*, 2015). Such waste materials are basically made up of lignin, cellulose and hemicellulose the structures of these constituents are displayed in Figure 1.1 to 1.3. The aforementioned basic components usually account for exchange and complexation properties of agricultural waste adsorbents (Ofomaja and Ho, 2007). Although these adsorbents have shown promising results for the removal of pollutants from wastewater, there are still limitations encountered in their use including their low uptake capacity when used in their raw (untreated or modified) form and the release of organic components leading to a high chemical and biological oxygen demand and total organic carbon (Abdolali *et al.*, 2014).

To overcome these limitations, lignocellulosic materials are usually chemically activated to improve their properties and performance using several types of chemical reagents including basic solutions such as sodium hydroxide, calcium hydroxide and sodium carbonate and inorganic acid solutions such as hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid and thioglycolic acid (Ngah and Hanafiah, 2008).

Chemical treatment of biomaterials does not only aid the extraction of soluble organic compounds from lignocellulosic materials thereby enhancing chelating efficiency, but also modifies the surface chemical properties of the final product. Djilali *et al.* (2012) observed that NaOH treatment of timber sawdust not only permitted the extraction of hemicelluloses and most of the lignin but also allowed the conversion of the polyol structure into a negatively charged cellulose-based material. Dawood and Sen (2012) treated pine cone biomass with HCl and observed that while the surface area increased, the mean particle size decreased when compared to the untreated samples. Therefore, treatment of lignocellulosic materials with an acid or basic solution will not only modify the chemical composition of the material but also lead to the formation of new functional groups in the form of hydrolysis or saponification for existing chemical compounds (Marshall and Johns, 1996; Dhakal *et al.*, 2005; Lu *et al.*, 2009).

Among the several mentioned methods that are used for the removal of pollutants in effluents, adsorption methods using agricultural waste materials have gained popularity (Ofomaja and Ho, 2007; Miretzky and Cirelli, 2010; Abdolali *et al.*, 2014; Gupta *et al.*, 2015). However, there is a need to develop cheaper and more effective adsorbent materials for the removal of trace metals from water sources.

This need can be addressed by exploring alternative biosorbents such as *Macadamia* nutshells.

South Africa is the third largest producer of *Macadamia* nuts in the world after Australia and Hawaii (Mogala, 2014). As the growth rate of *Macadamia* plantations steadily increases so also is the accumulation of *Macadamia* shells (Moodley *et al.*, 2007; Mogala, 2014). There appears to be no real use for waste *Macadamia* nutshells except for road compaction in farms and as a source of heat. Therefore, this study seeks to investigate the efficiency of using different chemically modifications of *Macadamia* nutshells as efficient adsorbents for the removal of selected trace metals from aqueous solution.

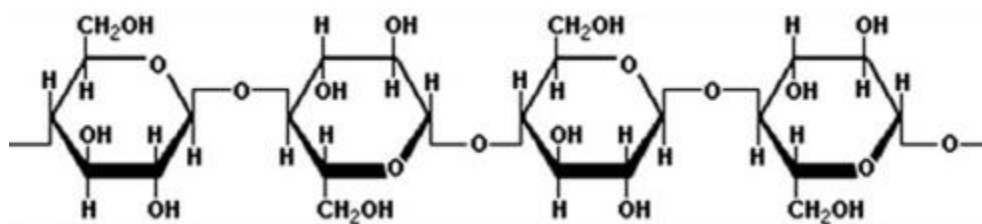


Figure 1.1: Structure of cellulose (Bajpai, 2016)

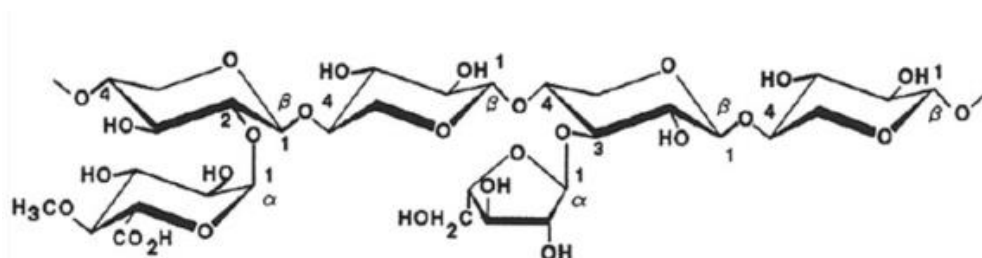


Figure 1.2: Structure of hemicellulose (Bajpai, 2016)

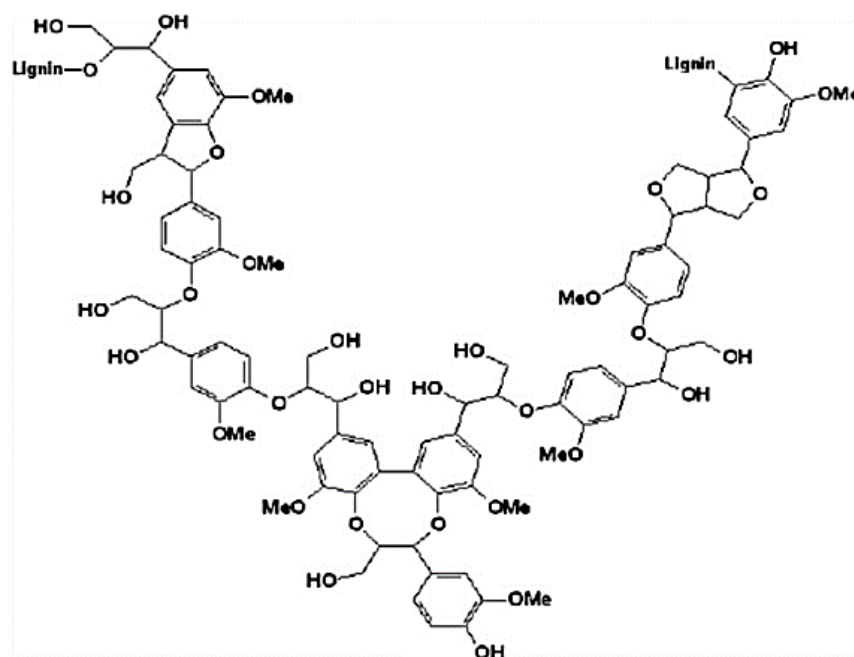


Figure 1.3: Structure of lignin (Bajpai, 2016)

1.2 Purpose of study

Rapid industrialization and urbanization have led to an increased use of trace metals resulting in huge waste disposal into the environment and creating a flux of metallic substances into the aquatic environment. Trace metals are emitted into the environment in quantities that are a risk to human health and the aquatic ecosystems due to their toxic and carcinogenic nature. Hence, it is important to remove these trace metals from wastewaters before transport and recycling into the natural environment. Adsorption methods employing readily available agricultural waste materials are a very promising solution to the removal of toxic trace metals from the environment. Using agricultural waste materials in their raw form poses a threat to the environment due to leaching of soluble organic compounds leading to high oxygen demand. Hence, in this study, various chemical modifications of *Macadamia* nutshell were used to remove selected trace metals from wastewater.

1.3 Justification

It is known that agricultural waste biomaterials such as shells, bark, pit etc, can be used as biosorbents for the removal of toxic trace metals or organic pollutants from aqueous solutions through adsorption technology. These plant-based materials are known to contain lignin, cellulose and hemicellulose as part of their core structure which accounts for complexation and exchange properties with metals (Ho and Ofomaja, 2006). Application of biosorbents in their pristine form may result in leaching of some plant components and contribute to high chemical and biological oxygen demand in water (Abdolali *et al.*, 2014). Therefore, biomaterials need to be stabilized through a process of chemical modification to prevent leaching out of components and to increase their metal removal efficiency. Adsorbents based on *Macadamia* have not been extensively explored for the removal of trace metals such as chromium, cadmium, cobalt, and copper from aqueous solution, according to author's knowledge.

Chapter two

2. Literature review

2.1 Trace metals of interest

Trace metals are defined as metals that have high density, high atomic weight, or high atomic number. Trace metals of interest in this study were the hexavalent chromium, copper, cobalt and cadmium. The selected trace metals are toxic to the biota and humans. Trace metals may accumulate in soil, air, and water, as reported by Nazir *et al.* (2015). The accumulation of trace metals in soil, water, and air may result in harmful effects on aquatic life and humans through the consumption of contaminated products from the soil, water, and air. Chromium, copper and cobalt are considered essential nutrients at trace levels but cadmium is a non-essential element (IARC, 1994). Nonetheless, excess consumption of the aforementioned metal nutrients can be toxic.

2.1.1 Chromium

Chromium in an aqueous environment is mainly present in its two most stable oxidation states, *viz.*, the hexavalent chromium [Cr(VI)] and the trivalent chromium [Cr(III)]. Cr(III) is found naturally in rocks, plants and soil, while Cr(VI) is rarely found in nature and is toxic (Gardea-Torresdey *et al.*, 2000). The main sources of Cr(VI) in drinking water are of anthropogenic origin including discharges or leakages from steel and pulp mills, and from a number of industries including: paint and pigments, textile, electroplating, canning, chrome plating, leather tanning, cement dyeing and erosion of natural deposits of chromium (III) (Parvathi and Nagendran, 2007). The two forms of

chromium have distinct toxicity levels, with Cr(VI) being highly toxic while Cr(III) is a micronutrient at low concentrations. Cr(VI) is more mobile and bioavailable than Cr(III), it is classified as a priority pollutant with carcinogenic actions (Muthukumaran and Beulah, 2011). Therefore, the priority should be to remove Cr(VI) from the water bodies or reduce it to its less harmful state of Cr(III) (Miretzky and Cirelli, 2010). Cr(III) exhibits the following species, the hydrated trivalent chromium $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ or the chromium hydroxide complexes $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ or $\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4^+$, whereas Cr(VI) species are the chromate CrO_4^{2-} , hydrogen chromate HCrO_4^- and dichromate $\text{Cr}_2\text{O}_7^{2-}$ (Kalidhasan *et al.*, 2016). The pH of the solution also plays a crucial role in the toxicity and the type of species that may be found in the aqueous environment.

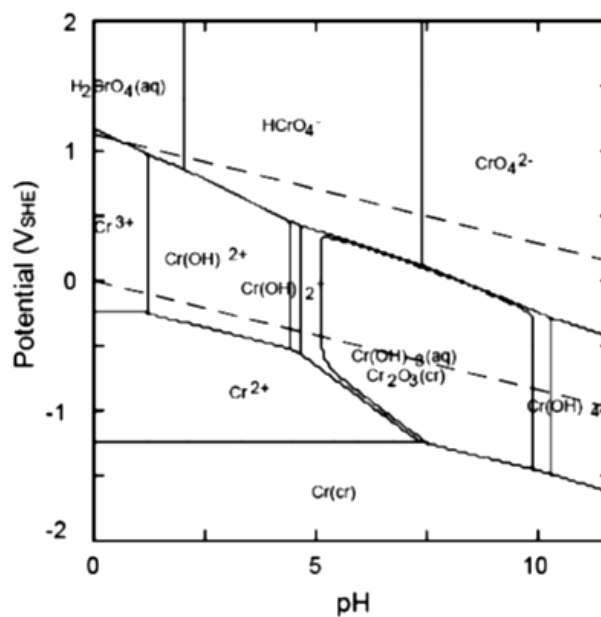


Figure 2.1: Eh-pH diagram of stability of different chromium species in an aqueous system (Ball and Nordstrom, 1998).

The diagram showing the stability of various chromium species in aqueous solution is given in Figure 2.1 while Figure 2.2 demonstrates the speciation of chromium

compounds. Figure 2.1 shows that the predominance of chromium species depend on their redox potentials and pH. At high concentrations, all compounds of chromium are toxic and may cause epigastric pain, nausea, vomiting and severe diarrhea (Selomulya *et al.*, 1999).

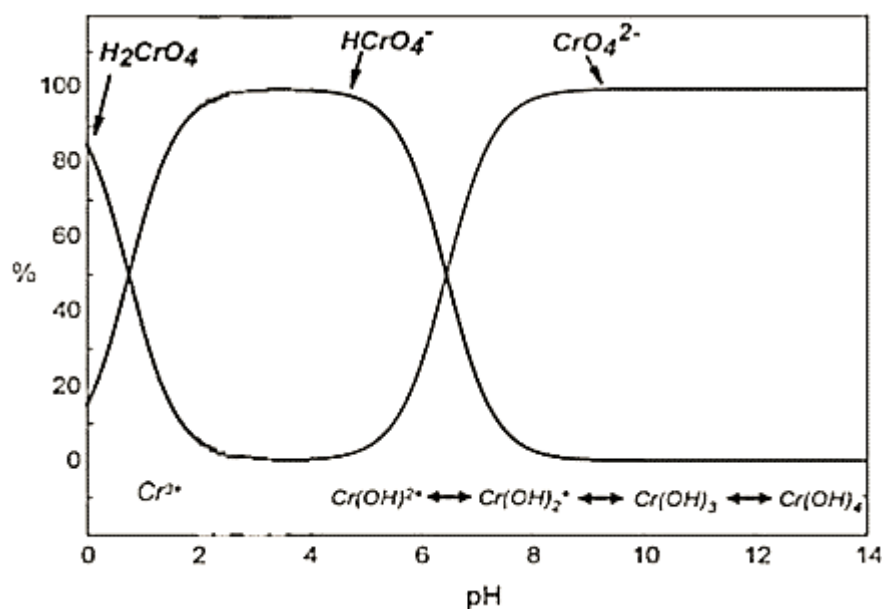


Figure 2.2: Speciation distribution diagram of Cr(III) and Cr(VI) in aqueous systems (Hagendorfer and Goessler, 2008).

2.1.2 Copper

Copper is considered as a trace element or an essential element because it is responsible for proper development of bones, tissues and the synthesis of enzymes by using protein as a mobility mode to get to their targeted organisms (Fraga, 2005). However, accumulation of copper ions in the human body may lead to brain damage and kidney complications (Gaetke and Chow, 2003). Excessive Cu(II) ions deposited in the liver may result in vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure (Akar *et al.*, 2009).

Copper has been used for a long time in the electronic industry because of its great properties such as electrical conductivity, ability to be stretched into a wire and ability to manage the very high amount of heat, and it is also used in the production of alloys. (Fornari and Abbruzzese, 1999; Cuppett *et al.*, 2006) reported that the solubility of copper in solution was dependent on the pH of the solution since it becomes more insoluble as the pH is increased. At $\text{pH} < 6$, the most dominant species of copper is the free cupric ion and the soluble copper complexes, while at $\text{pH} > 6$ the dominant species are the insoluble copper complexes as shown in Figure 2.3.

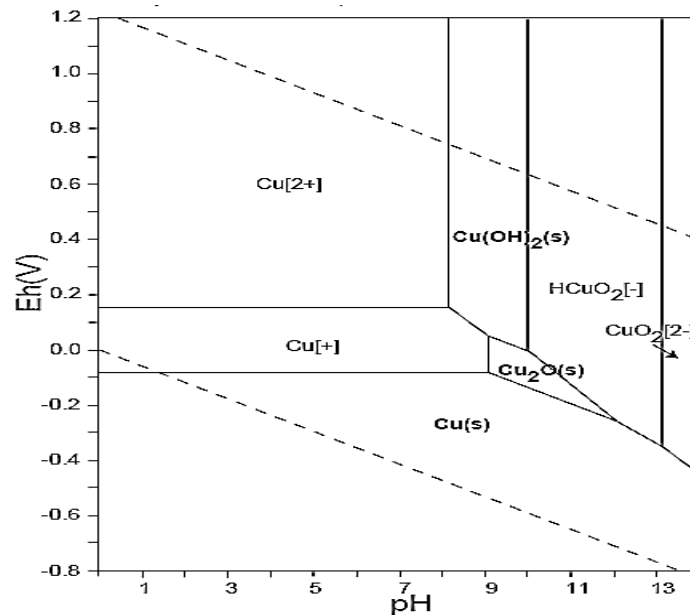


Figure 2.3: Eh-pH diagram of stability of different copper species in an aqueous system (Takeno, 2005).

2.1.3 Cobalt

Cobalt is an essential nutrient since it is interconnected with vitamin B12 and plays a role in the accurate functioning of the brain and nervous system (Abbas *et al.*, 2014). Overexposure to cobalt might lead to human health impediments such as

genetic mutations, cancer, liver damage, and heart problems (Nadaroglu and Kalkan, 2012).

Cobalt and its compounds have a widespread range of applications such as in stellite alloys for the usage in nuclear power plants (Collins and Kinsela, 2010). Additional applications are in paint, electroplating, electrical, and metallurgy industries (Singh and Shukla, 2016). Improper disposal of the waste from such industries may be the source of cobalt in water bodies. Similar to other metals, cobalt exists in different forms in aqueous solutions of various pH levels. At $\text{pH} < 6$, Co(II) is the most dominant species, while Co(OH)^+ predominates at pH 6 to 10. Between pH 8 and 10 Co_3O_4 is most prevailing while Co(OH)_2 and CoOOH are the most dominant species at pH 10-12 (Collins and Kinsela, 2010). A diagram showing cobalt speciation is displayed in Figure 2.4.

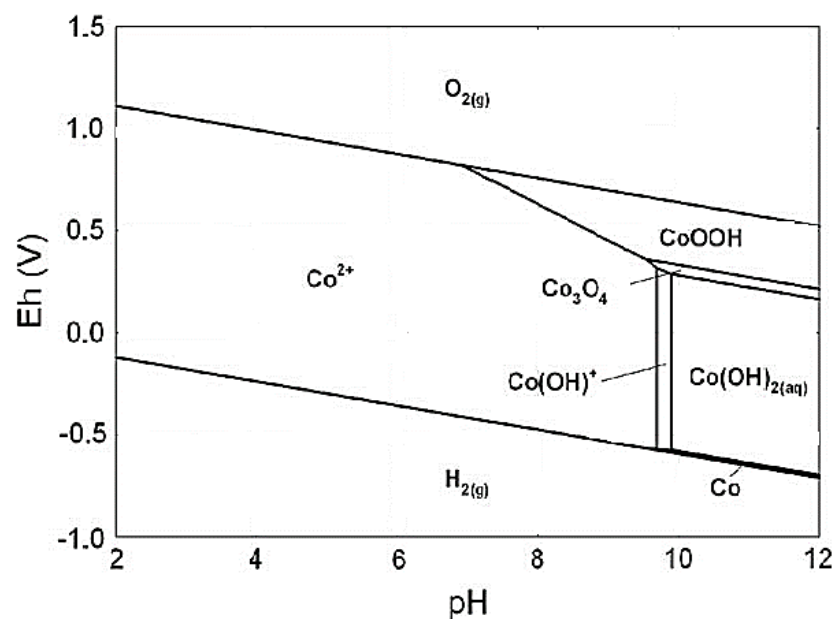


Figure 2. 4: Eh-pH diagram of stability of different cobalt species in an aqueous system (Collins and Kinsela, 2010).

2.1.4 Cadmium

Unlike chromium, copper, and cobalt as previously pointed out, cadmium is well-thought-out as a non-essential metal, contributing no part in the normal functioning of the human body (IARC, 1994). Cadmium is a significantly unique trace metal for it is predominantly produced as a by-product from zinc processes. Intensification in zinc production has led to a subsequent increase of cadmium production. Other sources of cadmium production include nickel-cadmium batteries (Fernandes *et al.*, 2012), steel production and electroplating sludge (Wang *et al.*, 2017). The toxicity of cadmium is accredited to its bioaccumulation and persistent nature. In humans, cadmium exposure may result in liver, kidney, stomach and prostate cancer (Waalkes, 2003).

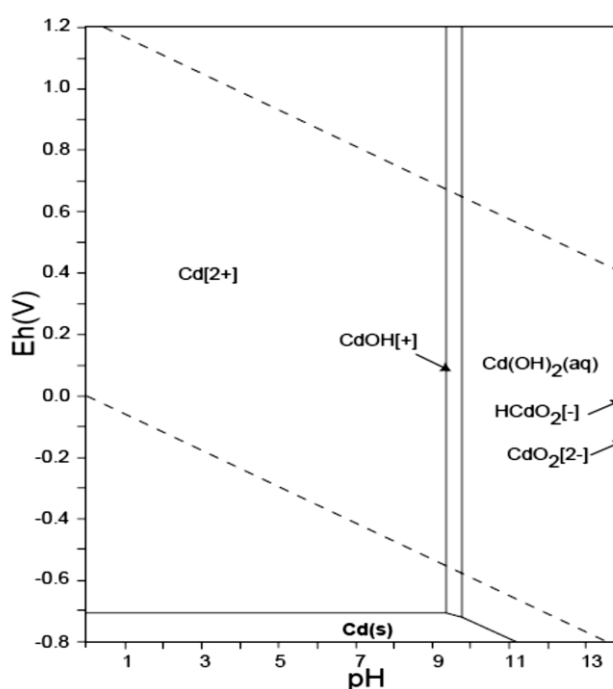


Figure 2. 5: Eh-pH diagram of stability of different cadmium species in an aqueous system (Takeno, 2005).

In aqueous solutions, cadmium may exist in different forms including free metal ion (Cd^{2+}) and several hydroxides such as CdOH^+ , Cd(OH)_2 , Cd(OH)_3^- , and Cd(OH)_4^{2-} . The solubility decreases with an increase in the concentration of

hydroxide ions (Ryan *et al.*, 1964). The speciation diagram of cadmium is shown in Figure 2.5.

2.2 Methods for trace metal removal from aqueous media

Efforts have been made to develop techniques or methods for the removal of trace metals from different matrices including soils, sediments, sludge and aqueous solutions. The methods include chemical precipitation (Gunatilake, 2015), membrane filtration (Tang *et al.*, 2013), electrochemical elimination (Khandegar and Saroha, 2013) etc.

2.2.1 Chemical precipitation

Chemical precipitation is a technique used for heavy metal removal from aqueous solution by means of the formation of a chemical precipitate. The technique is mostly suitable for large volumes of heavy metals that have low concentration levels (Gunatilake, 2015). The success of the aforementioned method depends on the adjustment of the solution pH, temperature and the addition of solvents, salts and polymers (Ayres, Davis and Gietka, 1994). The precipitation reaction is achieved by introduction of a suitable alkaline or sulfide solution, then the resulting precipitate is separated from the solution (Matis *et al.*, 2004). Ramakrishnaiah and Prathima (2012) described the use of sodium metabisulphite as a reducing reagent for the reduction of Cr(VI) to Cr(III). This was followed by precipitating the Cr(III) with a combination of sodium hydroxide and calcium hydroxide. The results showed that total chromium was removed from the synthetic and industrial effluent. However, the technique comes with shortcomings such as the generation of large amounts of chemical sludge (Acheampong, Meulepas and Lens, 2010),

and the re-dissolving of amphoteric metals as the pH levels are altered (Chen *et al.*, 2009).

2.2.2 Membrane filtration

Membrane filtration is a technique that is used to remove metal ions from solution by trapping the metal ions in a certain type of membrane. The method is reliant on the solution pH, metal ionic strength, initial metal concentration and surfactants. Specific techniques of membrane filtration include reverse osmosis (Tang *et al.*, 2013), electrodialysis (Sadrzadeh *et al.*, 2008) and nanofiltration (Al-rashdi *et al.*, 2013).

Yen *et al.* (2017) reported a comparison study on two types of membrane fibers. The filtration-ultrafiltration-reverse osmosis (FF-UF-RO) and the sand filtration-electrodialysis reversal (SF-EDR) on wastewater purification. It was found that the FF-UF-RO membrane was more suitable for water purification than the SF-EDR membrane since it had low operational cost. A blend of membranes consisting of polyurethane and cellulose acetate was used for the removal of hexavalent chromium from solution (Riaz *et al.*, 2016). It was described that the blend had a number of pores on its surface and effective removal was at pH 3 and 0.4 MPa of pressure.

Despite the reported success of the blend membrane, a comparison of the polyurethane membrane and cellulose acetate membrane used individually for Cr(VI) removal was not evaluated. This would have shown whether the blend demonstrated any advantage over the individual membranes. The technique has limitations such as membrane lifetime, fouling, insufficient rejection, chemical resistance and continued treatment after filtration (Van der Bruggen *et al.*, 2008).

2.2.3 Electrochemical technology

The electrochemical technology involves the separation of metal ions from solution by electron deposition on a cathode. Then, the metal is recovered in its elemental state. The electrochemical technique is comprised of electrocoagulation (Khandegar and Saroha, 2013) and electroflotation (Bhaskar and Khangaonkar, 1984). Aoudj *et al.* (2015) described the use of a combination of electrocoagulation and electroflotation for the removal of hexavalent chromium and fluoride from acidic semiconductor effluents. It was reported that the reduction of Cr(VI) took place during the electrocoagulation process (step one) and simultaneously the fluoride was undergoing coagulation. This was followed by clarification during electroflotation (step two). A combination of iron and aluminum plates were used as an anode and stainless steel was used as a cathode. It was reported that the iron plates were responsible for the removal of Cr(VI) and the aluminum plates were responsible for fluoride removal. The disadvantage of the method is the high cost of electricity that it requires for operation (Fu and Wang, 2011).

2.3 Adsorption

Adsorption is a phenomenal occurrence taking place at the surface of an adsorbent material where there is an accumulation of an adsorbate at a surface of an adsorbent or accumulation of adsorbate at the interface between two phases. Adsorption is mostly an exothermic process achieved using the forces of attraction between the adsorbent and adsorbate. Adsorption of adsorbate can be through physical or chemical interactions (Tutu *et al.*, 2013).

2.3.1 Physical adsorption

Physical adsorption or physisorption occurs when inter-molecular attractive forces (Van der Waals forces) between adsorbate and adsorbent are greater than those between adsorbate molecules. The physisorption is relatively quicker even though diffusion into pores may be time-consuming and mostly begins as a monolayer. Multilayer adsorption is also possible with physisorption. The porosity of the adsorbent is more important for this type of adsorption than the surface area. That is, maximum adsorption capacity is governed by pore volume and pore size. In addition to pore volume and pore size properties, the activation energy can be used as a parameter to get information about the type of adsorption or interaction taking place between adsorbate and adsorbent. For an adsorption reaction to being classified as physical adsorption, the activation energy must be between 5–40 kJ/mol (Boparai *et al.*, 2011).

Tutu *et al.* (2013) reported the physisorption of Co(II), Mg(II), Mn(II), and Zn(II) on the surface of a silica polyamine composite. The physical attraction was attributed to the activation energy of the reaction which was 14.78, 5.104, 19.792, and 16.04 kJ/mol for Co(II), Mg(II), Mn(II), and Zn(II), respectively. However, the structural and surface properties of the silica polyamine composite were not provided.

2.3.2 Chemical adsorption

Chemical adsorption (chemisorption) is a process where a chemical bond is formed between the adsorbate and the adsorbent. This could be through the transfer and sharing of electrons which result in the change of the state or form of the adsorbate. It is not easy to reverse this reaction and high temperatures may result in the breaking of the bond formed. The subsequent chemical bond formed between

adsorbate and adsorbent has all the attributes of a chemical bond and normally it is much stronger than that of physical adsorption which involves Van der Waals forces (Clark, 1974).

Chemisorption is dependent upon the number of adsorption sites that are present on the surface of the adsorbent where the metal ions get to bind. For chemisorption to take place high activation energy may be required. When the activation energy of an adsorption reaction is between 40–620 kJ/mol then that reaction is classified as a chemisorption reaction (Tutu *et al.*, 2013). The aforementioned authors also described the chemisorption of U(VI) onto silica polyamine composite. The chemisorption classification was attributed to the activation energy of the reaction which was 54.61 kJ/mol.

2.4 Types of adsorbents

An adsorbent is a material having a surface with pores that can attract substances to its surface. In recent years, the need for safe and economical methods for the elimination of trace metals from contaminated water has directed research interest toward the production of low-cost alternatives to commercially available activated carbon and various polymers. The use of natural polymers as adsorbents for pollutants has attracted widespread attention because of their unique chemical and adsorptive properties (Farrell and Breslin, 2004). Recently clinoptilolite zeolite was employed as an adsorbent for the removal of different metal ions (Cu(II), Cr(III) and Fe(III)) from the graphic industry sample. The zeolite material exhibited high percentage removal of Cu(II), Cr(III), and Fe(III) equalling to 95.4%, 96.0%, and 85.1%, respectively (Zanin *et al.*, 2017).

Activated carbon is another type of commonly used adsorbent for the removal of metal ions from aqueous samples due to the unique physical and chemical properties which include high surface area, large pore volume and easiness of the functional groups modifications. Activated carbons can be produced from a wide range of agricultural materials (Treviño-Cordero *et al.*, 2013). Activated carbon derived from mango kernel activated with H_3PO_4 was reportedly used as an adsorbent for Cr(VI) removal from aqueous solution (Rai *et al.*, 2016). The activated carbon had a carbon content of 78.56% which was significantly higher than the 44.71% of the raw mango kernel. The activated carbon was reported to have a BET surface area of $490.43 \text{ m}^2/\text{g}$, an average pore size and particle size of 38.9 nm and 781.5 nm, respectively. The carbon was reported to have an adsorption capacity of 7.8 mg/g for Cr(VI) (Rai *et al.*, 2016). Apart from the carbon content, the other results were not compared with the ones of the raw mango material. However, the adsorption capacity was related to other published results of activated carbons such as coconut tree sawdust 3.46 mg/g (Selvi, Pattabhi and Kadirvelu, 2001), and maize corn cob 0.28 mg/g (Garg *et al.*, 2007). The mentioned capacities remain relatively lower than that of the mango kernel activated carbon, making it competitive.

Despite the numerous other sources of adsorbents for trace metal removal, agricultural waste materials remain the mostly used adsorbents. Mainly because of their abundant availability in nature, unique functional groups, and cost-effectiveness. The cost of an adsorbent is of great importance for adsorption process but is not the only determining factor, the agricultural waste material comes with numerous advantages such as high efficiency for low metal concentrations, increased metal recovery (Nguyen *et al.*, 2013). However, at high metal ion

concentration biosorbents tend to have poor performance particularly if they are used in their raw or untreated form. The humidity, climate and soil type where agricultural materials grow influence their properties such as the adsorbent density and functional groups present.

Therefore, in attendance to what has been discussed, it is a vital requirement that all potential sources of economic agro-based adsorbents be explored and their feasibility for the removal of trace metals be studied in detail (Hegazi, 2013).

2.4.1 The selection of agricultural waste adsorbents

Agricultural waste adsorbent material such as leaves, bark, shells, roots, pit, twigs etc, contain a host of organic and inorganic compounds such as cellulose, hemicellulose, lignin, tannins, saponins, alkaloids, proteins and minerals. These compounds contain various functional groups that could interact with pollutants like metal ions through complexation and valence electron sharing. The aim is not to kill the plant to get the required adsorbent, therefore it is important that researchers consider investigating parts that the plant normally shed off as waste. For example, after recovering the fruit the nutshells become a waste material. Thus, their use as adsorbents is justified.

There is a general consensus among researchers that the selection of agricultural waste materials as biosorbents should be based on several requirements, including abundance, high cost-effectiveness, easy desorption, high regeneration capability, and negligible release of unexpected compounds into aqueous solutions (Nguyen *et al.*, 2013). The present study explored the use of *Macadamia* nutshells as an adsorbent for the removal of hexavalent chromium from aqueous solution.

2.4.2 Adsorbents derived from agricultural waste materials

The physicochemical structure and adsorption properties of natural adsorbents vary depending on the initial material used (Sudaryanto *et al.*, 2006). Adsorbents with macroporous structures can be produced from materials with high lignin content, like grape and cherry seeds. Adsorbents with a high content of micropores can be obtained from almond and apricot seeds which have high cellulose content. Nevertheless, the formation of pores is especially affected by the type of activating agent used in chemical reaction (Wu *et al.*, 2011).

Numerous adsorption studies on the use of agricultural waste material as adsorbents have concentrated on untreated and treated agricultural waste such as papaya wood (Saeed *et al.*, 2005), carob shells (Farnane *et al.*, 2017), maize stover (Guyo *et al.*, 2015), peanut husks (Rozumová *et al.*, 2016), *Swietenia mahagoni* shells (Rangabhashiyam and Selvaraju, 2015), *longan seed* (Yang *et al.*, 2015), corn stock (Chen *et al.*, 2012), grapefruit peelings (Rosales *et al.*, 2016), sugarcane bagasse (Garg *et al.*, 2009), rice straw (Hsu *et al.*, 2009), wheat bran (Kaya *et al.*, 2014), etc. It has been established that even though untreated agricultural waste material based adsorbents have been used successfully, the challenge of low adsorption capacities associated with such materials remains a critical issue and is the basis for current research involving modifications with various activating agents.

2.4.3 *Macadamia* nutshells

Macadamia nutshells have been used in fossil fuel during the co-pyrolysis of polyethylene terephthalate. It was reported that the *Macadamia* nutshells catalyzed the degradation of polyethylene terephthalate and the resulting combination

yielded an increase in char formation due to the cross-link formed between the polymer and the nutshells (Ko *et al.*, 2014). Apart from being used in fossil fuel *Macadamia* nutshells have found use in the adsorption of pollutants from aqueous solutions. Pezoti Junior *et al.* (2014) reported the adsorptive capability of *Macadamia* nutshells in the removal of methylene blue. The *Macadamia* nutshells were converted into activated carbon using microwave assisted pyrolysis and ZnCl_2 as an activating agent. It was reported that acid functional groups were most dominant on the nutshell surface and the monolayer adsorption capacity was found to be 194.7 mg/g for methylene blue.

The adsorption of phenol from aqueous solution using activated carbon derived from *Macadamia* nutshells has been reported by Rodrigues *et al.* (2013). A spontaneous and exothermic adsorption process was reported and the monolayer adsorption capacity was found to be 341 mg/g for phenol.

Poinern *et al.* (2011) reported the adsorption of a gold complex using activated carbon derived from *Macadamia* nutshell. The activation was done in a two-step process: firstly the nutshells underwent carbonization in an inert environment followed by physical activation under a carbon dioxide atmosphere. Secondly, it was reported that the capacity of the *Macadamia* nutshells was comparable to that of coconut-derived activated carbon which was being used in the recovery of gold. The *Macadamia* nutshells are promising adsorbents for the removal of pollutant (Pakade *et al.*, 2016) but there is a lack of literature on the use of *Macadamia* nutshells as an adsorbent for trace metal ion removal. The few researchers that have reported the use of *Macadamia* as adsorbents for trace metals have not reported the use of the nutshell in its native or raw form but they have used them as a source of activated carbon.

The lack of available literature on non-activated carbon *Macadamia* nutshells may be a consequence of the scarcity of nut trees as they grown in subtropical conditions and the difficulty in crushing the nutshells into a fine powder for an increased surface area. This study seeks to contribute to the much-needed research information on native or raw *Macadamia* nutshells. A part of this research has been published by Pakade *et al.* (2016) where raw *Macadamia* nutshells were investigated as an adsorbent for hexavalent chromium removal. The effect of the different chemical treatment of the nutshells has been detailed in Chapter five.

2.5 Modification of agricultural waste materials

Various factors such as specific surface area, pore size distribution, pore volume, and the presence of surface functional groups influence the adsorption capacity of adsorbents. Adsorbents derived from the agricultural waste material can be modified to have the desired physical and chemical attributes to enhance their affinities toward metal ion uptake from aqueous solutions. Usually, adsorption capacity increases with increase in specific surface area due to the availability of a number of adsorption sites, while pore size and micropore distribution are closely related to the composition of the adsorbents and the type of biomass raw material supplied for their synthesis (Ruthven, 1984).

To improve surface properties, materials are sometimes pretreated by physical means including heating/boiling, freezing/thawing, vacuum and freeze-drying, autoclaving and mechanical disruption. Chemical pretreatments used for raw biomaterial modification include treating the biomaterial with detergents, inorganic acid or alkali solutions. The pretreatments could modify the surface characteristics/functional groups either by removing or masking the functional groups or by

exposing more metal binding sites. Following pretreatments, the materials could further undergo chemical modifications by treatment with various organic and inorganic compounds, such as organic acid, caustic, methanol, formaldehyde, etc. (Vieira and Volesky, 2000).

2.5.1 Chemical modification of adsorbents

Suksabye and Thiravetyan (2012) chemically modified coir pith for the adsorption of Cr(VI) from electroplating wastewater. The modification was achieved by grafting acrylic acid on the surface of coir pith. Scanning electron microscopy images exhibited an uneven surface for the modified than the unmodified coir pith. It was also established by FTIR spectral analysis that modified coir pith showed the greater intensity of carbonyl groups. The aforementioned method resulted in a more effective adsorbent than the unmodified one. Chemically modified and unmodified rice husks were used for the removal of trace metals from aqueous solution (Kumar and Bandyopadhyay, 2006). Elsewhere, chemical modifications were achieved using sodium hydroxide, sodium carbonate, and epichlorohydrin to enhance the adsorption capacity of cadmium. The base treatment using NaOH removed base-soluble materials on the rice husk surface and that might enhance adsorption property resulting in low removal (Ngah and Hanafiah, 2008). Earlier Teixeira Tarley, Costa Ferreira and Zezzi Arruda, (2004) reported that the adsorption of Cd was almost doubled when rice husks were modified with NaOH. The discrepancies could be attributed to different chemical constituencies of the plants resulting from climatic conditions. According to Esteghlalian *et al.* (1997), pretreatment using a dilute acid such as sulfuric acid can attain high reaction rates and improve cellulose hydrolysis. Hydrochloric acid treated rice husks displayed lower adsorption capacity of Cd than the untreated rice husk (Kumar and

Bandyopadhyay, 2006). The reduced performance of hydrochloric acid treated rice husk was as a result of the protonation of the adsorption sites on the surface of the husk leaving the Cd ions in the solution phase owing to repulsion forces (Nghah and Hanafiah, 2008).

Spent grain acquired from brewery treated with NaOH and HCl was likewise utilized for the removal of Pb(II) and Cd(II) ions. The spent grain treated with NaOH displayed significantly enhanced adsorption of Cd(II) and Pb(II) ions, while the HCl treated presented lower adsorption capacity. The increase in adsorption of trace metal ions after base treatment was explained by the increase in a number of galacturonic acid groups after hydrolysis of o-methyl ester groups (Low *et al.*, 2000).

Even though most agricultural waste materials showed better efficiency when modified with a base, wheat bran treated with a dehydrating agent like sulfuric acid was more effective than its base treated derivative (Öze *et al.*, 2004). The treatment of wheat bran with sulphuric acid had a significant effect on the surface area of the adsorbent which eventually resulted in a better adsorption efficiency for copper ions (Özer *et al.*, 2004). Pretreating wheat bran with sulfuric acid increased the surface area due to the conversion of macropores to micropores (Özer and Pirinççi, 2006).

Chemical modification of cornelian cherry, apricot stone, and almond shells by using concentrated sulfuric acid for the removal of Cr(VI) has been reported (Demirbas *et al.*, 2004). All three types of agricultural waste materials showed the highest removal of Cr(VI) at pH 1. Adsorption was highly dependent on the initial metal concentration as the lowest concentration recorded fastest removal rate.

Nasernejad *et al.* (2005) used HCl treated carrot residues to remove trace metals such as Cr(III), Cu(II) and Zn(II) from wastewater. The acid treatment was performed to remove tannins, resins, reducing sugars and colored materials. According to Nasernejad *et al.* (2005), adsorption of metal ions onto carrot residues was possible due to the presence of carboxylic and phenolic groups which have cationic properties. Sulfuric acid was used to functionalize avocado seeds (Bhaumik *et al.*, 2014). It was reported that the removal of Cr(VI) was highly dependent on pH, with a maximum adsorption at pH 2. This was due to the fact that chromium exists in three forms in solution: HCrO_4^- at $\text{pH} < 6$, $\text{Cr}_2\text{O}_7^{2-}$ at $\text{pH} > 6$ and CrO_4^{2-} at low pH. Hydrogen chromate and dichromate were adsorbed at low pH and chromate was adsorbed at higher pH.

Rao *et al.* (2010) used *Foeniculum vulgare* a medicinal herb for the effective biosorption of Cd(II) ions. The maximum adsorption achieved was 92% at pH 4.3. It was reported that the biosorption was highly influenced by the concentration. The kinetic studies indicated that the reaction was endothermic and spontaneous following the pseudo second-order rate model.

Triethylamine modified corn stock was used to adsorb Cr(VI) from aqueous solution (Chen *et al.*, 2012). It was reported that when using the fixed bed method the adsorption capacity was increased by increasing the bed depth and decreased when the concentration and the flow rate were increased. The study did not compare the adsorption of raw and modified corn stock. There was no analysis to show the possible organic functional groups that are responsible for the interaction between the metal ions and the agricultural material. Ofomaja *et al.* (2015) reported the successful removal of cesium by adsorption onto pine cone functionalized with a combination of the toluene-ethanol solution. It was reported that the bulk density

of the raw pine cone decreased from 0.499 to 0.427 g/cm³ when the raw pine cone was treated with the toluene-ethanol mixture. This indicated that there may have been an increase in the opening of pore spaces in the modified pine cone. The chemical modification of the pine cone was able to improve adsorption properties of the raw pine cone such as the bulk density, because of the extraction of some of the organic compounds during the chemical modification.

2.6 Parameters influencing trace metal ion adsorption

The removal of trace metal ions from aqueous solutions by adsorbents is strongly reliant on adsorption parameters such as solution pH, initial metal ion concentration, the mass of adsorbent, and contact time.

2.6.1 pH of solution

The pH of a solution has a major influence on the adsorption of metal ions, since the adsorbent surface and the metal speciation gets affected by the change in pH of the system (Nouri *et al.*, 2007). At certain pH trace metals undergo hydrolysis forming complexes with water molecules. Some metals such as sodium(I) and potassium(I) do not hydrolyze, but the metals investigated in the current study do hydrolyze at different pH. The hydrolysis of Cr takes place at a pH range of pH 1 – 3 and Ni, Co, Zn, Cd, Cu, and Pb all hydrolyze at a pH range of about pH 6-8 (Baes and Mesmer, 1986)

Trace metal ions adsorption can be followed by solution pH variations because most of the metal ion's removal revolves around the isoelectric point or the neutral point. It is around this point that there is less interference from solubility and the non-polar adsorbents have great attraction for non-ionic material. Since other adsorbents have great attraction for H⁺ or OH⁻ ions, it means that metal ion

solubility and the adsorption capacity of the adsorbent will be affected (Eldridge *et al.*, 2015). The coulombic interaction between adsorbent and adsorbate has been reported by (Luef *et al.*, 1991), the results of such an occurrence were attributed to the electrostatic attraction between negatively charged surface moieties and positively charged metal ion species. Acid-treated carbons based on sawdust were tested for the removal of Cr(VI). The adsorption was reported to be reliant on the solution pH with an optimum pH of 3. Beyond pH 3 there was a decrease in the adsorption of Cr(VI). The maximum Cr(VI) adsorption at pH 3 was attributed to the presence of predominant anionic Cr(VI) species which are attracted to the protonated carbon surface through electrostatic attraction (Álvarez *et al.*, 2007).

The point of zero charge also contributes to the adsorption of trace metals. It is defined as the pH of the adsorbent was the number of positive charges on the surface equals to the number of negative charges. Pine cone with a point of zero charge (pH_{PZC}) of 7.49 when treated with NaOH resulted in decreased pH_{PZC} . The aforementioned materials were used as adsorbents for the removal of copper. The NaOH treated sorbents exhibited a high copper removal than the untreated material. The higher removal was ascribed to the increased number of negative charges imparted by the base treatment which gave rise to a decreased point zero charge (Ofomaja *et al.*, 2009).

2.6.2 Contact time

The effect of contact time in adsorption process is determined in order to ascertain when a particular sorbent will reach equilibrium during its application, it also aids in determining the residence time and reactor sizing. A number of factors contribute to the time it takes for an adsorption process to attain equilibrium.

Factors such as the number of adsorption sites present on the surface of the adsorbent, the size of adsorbent, the mass of adsorbent, initial concentration, and pH of the metal ion solution (Aksu and Kutsal, 1991).

Sepehr *et al.* (2014) investigated the use of pumice and surface modified pumice for the adsorptive removal of Cr(VI) from aqueous solution. It was concluded that the contact time influenced the removal of Cr(VI) on both the raw and modified pumice. For the first 150 min, the uptake of Cr(VI) was high for both materials with the modified pumice having a higher uptake. After 150 min the uptake as a function of time was reported to be non-significant, hence 150 min was used in the succeeding experiments as the optimum time.

2.6.3 Initial concentration of metal ions

Ndlovu *et al.* (2011) suggested that the sorbate–sorbent equilibrium of an adsorption reaction can be determined by relating the initial sorbate concentration with the mass of the sorbent and thus be able to overcome the resistance to mass transfer between the sorbate and sorbent. Generally, as the initial sorbate concentration is increased its subsequent removal also increase to a point where all the adsorption sites have been fully occupied by sorbate ions. Then a decrease in sorbate removal is experienced due to higher sorbate ratio to adsorption sites available. Thus, understanding at which point will the adsorption sites be fully occupied at a particular initial sorbate concentration and sorbent mass is important in overcoming the resistance to mass transfer. Dima *et al.* (2015) observed that the adsorption capacity of chitosan increased as the initial concentration of Cr(VI) was increased. This was attributed to the availability of adsorption sites which were not fully occupied as the initial concentration of Cr(VI) was increased.

2.6.4 Mass of adsorbent

Investigating the effect of adsorbent mass in adsorption studies is paramount in order to avoid the use of excessive sorbent and also to understand what minimum adsorbent mass is required for the uptake of pollutants. For economic reasons, use of excess adsorbent mass could lead to loss of resources. For industrial application the solid-liquid ratio, loosely translated as the dosage is imperative. Adsorbent mass is closely interrelated to the number of adsorption sites present on the surface of the adsorbent. Numerous studies have shown that an increase in adsorbent mass (dosage) results in an increase in metal ion removal (Dehghani *et al.*, 2016; Labidi *et al.*, 2016). The increase is ascribed to the increased number of adsorption sites as the mass is increased (Charles and Odoemelam, 2010). The relationship between the adsorbent mass and the percent metal ion removal is reported to be interlinked. Dehghani *et al.* (2016) observed that when the mass of the adsorbent was increased the percent metal ion also increased. This was ascribed to a higher surface area as the adsorbent mass was increased resulting in more adsorption sites available for metal ion adsorption.

2.6.5 Temperature

Temperature studies are used to investigate the thermodynamics of the adsorption process. Mekonnen *et al.* (2015) reported the thermodynamics of the adsorption of Cr(VI) using local adsorbents from Ethiopia. The temperature had an impact on the adsorption of Cr(VI) because as the temperature was increased from 20°C - 40°C, the adsorption of Cr(VI) also increased. The authors attributed the increase to the enhanced intraparticle diffusion and the possibility of the formation of new adsorption sites induced by increased temperature. The Cr(VI) removal was

reported to be feasible and spontaneous because of negative values of the standard Gibb's energy.

The nature of the reaction can also be determined by temperature studies. In the adsorptive removal of Pb(II) and Cd(II) using wild *Cocoyam* biomass, it was reported that at low temperatures the adsorption was mostly favored due to the physisorption interaction between adsorbent and adsorbate, and the reaction was classified to be exothermic (Wassie and Srivastava, 2016). The boundary layer thickness also assists in binding the metal ions to the surface of the adsorbent and it is affected by temperature. At high temperatures, the boundary thickness decreased and result in the de-attachment of metals ions (Aksu and Kutsal, 1991).

2.7 Desorption and regeneration studies

Adsorbent regeneration or reusability experiments are done to study the capability of the adsorbent to be recycled and also to recover the precious metals. An adsorbent can be regenerated by using regenerating agents or metal desorbing eluents such as an acid, base, or chelating agents like ethylene diamine tetraacetic acid (EDTA) (Lata *et al.*, 2015). The significant characteristic of a regenerating agent is that it must be able to desorb the metal from the adsorbent surface and it must not damage the adsorbent (Das, 2010). NaOH was used to desorb arsenic from a manganese dioxide coated sand (Bajpai and Chaudhuri, 1999). It was stated that after multiple regeneration experiments arsenic was recovered to about 85–98.3%.

Dehghani *et al.* (2016) reported the adsorption of Cr(VI) from aqueous solution by treated newspaper waste. A maximum adsorption capacity of 59.88 mg/g at pH 3 was reported and HCl was used as a desorbing agent, about 72% of Cr(VI) was desorbed back into solution. However, only one cycle of desorption was

undertaken and this raised questions about the suitability of newspaper waste as an adsorbent. Also, the desorption mechanism was said to be due to the presence of H^+ ions on the surface of adsorbent which in this case the authors were looking at Cr(VI) being Cr^{6+} whereas it is known that Cr(VI) exists as an anion in aqueous solution.

Higher regeneration of an adsorbent used for trace metal ion adsorption is achieved when the acid solution is used instead of alkaline or natural eluents (Srivastava and Goyal, 2010). The main reason for such an occurrence has been attributed to the dissolution or desorption of cations favored under acidic conditions. The cations get displaced from the adsorbent surface because of high competition with H^+ ions (Zhou and Haynes, 2011). In general alkaline, regeneration is more preferential for the desorption of anionic species like Cr(VI) (Lata *et al.*, 2015).

Even though the agricultural waste material is being used for removal of trace metals from water systems the low adsorption capacities and non-element selectivity of this materials continue to be a problem. Hence, the current study seeks to address such issues by chemically modifying the surface of *Macadamia* nutshell with HCl and NaOH followed by grafting with acrylic acid.

Chapter three

3.1 Aims and objectives

The aims of this study were to prepare raw and chemically modified *Macadamia* nutshells powder and evaluate their abilities to remove Cr(VI), Cu(II), Co(II), and Cd(II) from aqueous solution.

The aims of this study were achieved by addressing the following objectives.

- I. Chemically modifying the raw *Macadamia* nutshell RMN with HCl and NaOH.
- II. Preparation of acrylic acid grafted biosorbents from the HCl and NaOH modified biosorbents to incorporate the carboxylic functional groups on the surface of the biosorbents.
- III. Study trace metal adsorption and desorption by the raw and modified biosorbents with particular emphasis on the effect of pH, initial adsorbate concentration, contact time, adsorbent dosage, temperature and presence of competing ions in solution.
- IV. Characterize all the biosorbents prepared using Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM) Brunauer, Emmett and Teller (BET), X-ray Diffraction (XRD) and carbon, hydrogen, nitrogen plus sulfur analysis (CHNS)
- V. Study the equilibrium, thermodynamic and kinetic aspects of the adsorption processes using known models.

3.2 Research questions

- I. How will the chemical modification affect the physical and chemical properties of the *Macadamia* nutshells?
- II. Can the chemical modification provide selective removal of trace metal ions?
- III. Can the chemical modification improve the adsorption capacity and the removal efficiency?
- IV. Can the adsorbents be regenerated and if that is the case how many times can they be regenerated?
- V. Will the trace metal ions removal mechanism be the same or different for the prepared adsorbents?

3.3 Hypothesis

Surface treatment of agricultural waste biosorbents by means of an acid or a base will result in extraction of particular compounds from biosorbents. Consequently leading to development of a high surface area and higher metal ions removal. Grafting of acrylic acid on acid and base modified biosorbents will increase metal chelation and selectivity.

3.4 Research contribution to the study

The research explores the possibility of using *Macadamia* nutshells as biosorbents for removal of selected trace metals from aqueous solution. This research also provides information about physical and chemical properties of the *Macadamia* nutshells for better modification of the surface properties resulting in high

adsorption. Data regarding adsorption of trace metals under different conditions were generated leading to a proper understanding of adsorption mechanism.

Chapter four

4.1 Materials and chemicals

The *Macadamia* nutshells were donated by two local farms in Tzaneen (Eastern Produce Estates – SA (Pty) Ltd) and in Barberton (Danroc (Pty) Ltd), South Africa. Chemicals used were purchased from Sigma-Aldrich, Labchem and Merck (Johannesburg, South Africa). The stock solution was prepared by dissolving appropriate amounts of metal salt with ultrapure water. For chromium stock solution, pre-dried potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was dissolved in 1000 mL ultrapure water and for the mixed metals stock solution, $\text{K}_2\text{Cr}_2\text{O}_7$, cadmium chloride hemi(pentahydrate) ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and copper(II) sulfate anhydrous (CuSO_4) were all dissolved in a 1000 mL of ultrapure water. For a stock solution of coexisting anions, appropriate amounts of sodium chloride (NaCl), potassium dihydrogen phosphate (KH_2PO_4), ammonium nitrate (NH_4NO_3), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), potassium hydroxide (KOH) including $\text{K}_2\text{Cr}_2\text{O}_7$ were all dissolved in a 1000 mL of ultrapure water. Working solutions and calibration standards were prepared through serial dilutions of the stock solutions. The pH meter used for pH measurements was AD 111 pH meter from ADWA instruments and 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used for adjustments of pH. Solvents used were ethanol, methanol, benzene and acetone. 1,5-diphenylcarbazide was used as a complexing agent for the determination of Cr(VI) concentration. The ultrapure water that was used throughout the study was prepared from a LaboStar equipment supplied by Siemens (Warrendale, PA).

4.2 Adsorbent preparation

Stones and wood debris were handpicked from the shells and the nut residue inside the shells was scraped off manually, then the shells were rinsed with tap water and dried in an oven at 105°C for 24 h after which they were cooled to room temperature. Subsequently, the shells were crushed and sieved to a size fraction between 90 µm and 150 µm. The powder was soaked in ultrapure water then it was agitated for 3 h using a multi-channel stirrer, and then dried in an oven at 105°C for 24 h. The dried material was cooled in a desiccator and labeled raw *Macadamia* nutshells (RMN) or unmodified *Macadamia* nutshells. Different chemical methods were used to modify the surface of RMN, these methods included treatment with NaOH, HCl and grafting with acrylic acid.

4.2.1 Modification with hydrochloric acid (HCl) or sodium hydroxide (NaOH)

The HCl modification was done to remove acid soluble materials, where 250 mL of 0.1 M HCl was introduced into a beaker containing 20 g of RMN. The mixture was agitated for 3 h followed by vacuum filtration using the Whatman #4 filter paper. Excess or unreacted HCl was removed by rinsing the material with ultrapure water until a neutral pH. After rinsing the material was oven dried for 24 h at 105°C, thereafter the material was left to cool in a desiccator then labeled acid modified *Macadamia* nutshells (AMM). The same procedure was followed for NaOH modification, where 0.1 M NaOH was used in the place of 0.1 M HCl and the material was labeled base modified *Macadamia* nutshells (BMM). The base modification was done to remove base-soluble materials.

4.2.2 Carboxylic acid grafting to *Macadamia* nutshells

A method adapted from Suksabye and Thiravetyan, (2012) was used with modifications. About 20 g of AMM material was soaked in a 1000 mL of 0.5 M or 1 M or 2 M acrylic acid and 500 mL of 0.1 M HNO₃. The mixture was agitated for 30 min under inert conditions, then 25 mL of 0.00125 M ceric ammonium nitrate (CAN) solution was added and the contents were agitated for 3 h. The grafted material was separated from the mixture by means of vacuum filtration using Whatman #4 filter paper. The unreacted chemicals were rinsed off with ultrapure water until a neutral pH. The material was dried in an oven at 60°C for 24 h, and then cooled in a desiccator. The resultant material was labeled 0.5 GAM, 1 GAM and 2 GAM corresponding to 0.5 M, 1 M and 2 M acrylic acid grafting on AMM material, respectively. The same procedure was followed where AMM was replaced with BMM and labeling of the BMM grafted material followed the same pattern with 0.5 GBM, 1 GBM and 2 GBM corresponding to 0.5 M, 1 M and 2 M acrylic acid grafting on BMM material, respectively.

4.3 Biosorbent and adsorbate characterization.

The physical and chemical properties of *Macadamia* nutshells before and after adsorption, as well as the determination of trace metal ion concentration in solution, were completed through the use of diverse techniques such as the ones described from 4.3.1 to 4.3.8.

4.3.1 Fourier – transform infrared (FTIR) spectroscopy

PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer (Waltham, USA) was employed for the determination of organic functional groups present on the surface of the adsorbents that appear in the frequency range of 500–4000 cm⁻¹.

4.3.2 Carbon, hydrogen, nitrogen and sulfur (CHNS) analysis

The percentage of carbon, hydrogen, and nitrogen present in the biosorbents were quantified by a Thermo Flash 2000 series CHNS/O Organic Elemental Analyzer. This technique employs the oxidation reactions, was sample is subjected to high temperatures (1000°C) for combustion. This is done under the flow of constant oxygen based on the Pregl-Dumas method. During this process, the carbon undergoes oxidation to form carbon dioxide, while hydrogen is converted to water.

Similarly, nitrogen is converted to nitrogen oxide or nitrogen gas sulfur to sulfur dioxide. Excess oxygen is removed by flushing the combustion product. Ultimately the instrument detects the formation of CO₂, H₂O, elemental nitrogen and sulfur dioxide (Fadeeva *et al.*, 2008).

4.3.3 Thermogravimetric analysis (TGA)

The thermal stability of adsorbents was studied using a PerkinElmer STA 600 Simultaneous Thermal Analyzer (Waltham, USA). The analysis was accomplished under a nitrogen atmosphere, 3.2 bar pressure, 20 mL/min flow rate and at a heating rate of 10°C/min starting from zero to 900°C. Thermal analysis is a measure of the changes in the physical and chemical properties of a sample. A particular mass of the sample is put in a pan under controlled environment and heated up at a defined heating rate. The sample undergoes mass loss as a consequence of losing moisture and volatile components. The instruments record those changes as a function of temperature (Gallacher, 1998).

4.3.4 Scanning electron microscopy (SEM)

Scanning electron microscope incorporated with energy-dispersive X-ray spectrometer (SEM-EDS) from FEI Nova NanoLab FIB/SEM (Milpitas, CA) was used for surface morphological descriptions. The sample is subjected to a beam of energetic electrons in a process that produces different signals around the surface of the sample. As the electrons penetrate the sample particles will be emitted and that information will be collected by the detector. This provides morphological information of the sample such as surface texture, sample composition, and sample orientation (Kaur, 2015).

4.3.5 Ultraviolet-visible (UV–Vis) spectroscopy

The concentration of Cr(VI) was acquired on a UV–Vis spectrometer (T80⁺, Instruments) at a wavelength of 540 nm. For the determination of concentration via the UV-Vis spectrometer, Beer-Lambert law is assumed to follow the zero – order spectrum implicating that the correlation concerning concentration as well as amplitude is a linear connection. This relationship is principally expounded by the succeeding equation,

$$A = \epsilon bc \quad 4.1$$

where A is the absorbance, ϵ is the extinction coefficient (L/mol/cm), b is the path length of the sample (cm) and c is the concentration of the sample (mol/L) (Owen, 2000).

4.3.6 Atomic absorption (AA) spectroscopy

The atomic absorption spectrophotometer AA-700 from Shimadzu (Kyoto, Japan) was used to quantify trace metal ions concentration from solutions. The AA spectroscopy is a technique that uses a comparable principle as the UV-Vis spectroscopy in terms of concentration determinations. The concentration is calculated by the procedure of the Beer-Lambert law which can be described by the direct proportionality of absorbance plus concentration. This is achieved by first nebulizing the sample with air and nitrous oxide as oxidant gas and fuel gas, respectively. Thereafter, dissociation takes place and the sample is atomized at the same time ionization occurs due to extra energy from the flame (García and Báez, 2012).

4.3.7 Powder X-ray diffraction (PXRD)

The X-ray diffractions were obtained from an XRD-7000 X-Ray Diffractometer from Shimadzu (Kyoto, Japan). The X-ray diffraction employs X-rays or particles in motion which can be neutrons and electrons to study the structural properties of any material. Deductions on the amorphousness or crystallinity as well as the atomic d-spacing of a material can be made. This is done by beaming the powder sample with X-rays produced from an X-ray tube. These X-rays are converted into monochromatic radiation. Thereafter, the radiation is beamed at the sample, then the sample will interrelate with the incident rays and form constructive interference under circumstances appropriate to Bragg's law. The Bragg's law equates the wavelength of the radiation to that of the diffraction angle and the lattice spacing. Then the diffracted X-rays will be processed and counted through a range of 2 θ

angles. Under specialized conditions gases including liquids are also analyzed (Bunaciu *et al.*, 2015).

4.3.8 Brunauer, Emmett and Teller (BET) surface area measurements

The surface area measurements were obtained from a Micromeritics Flow Prep 060 from Tristar instrument employing nitrogen adsorption/desorption isotherms at -196°C.

4.4 Wet chemistry characterization

Some physical and chemical properties of the adsorbents cannot be done by using sophisticated instrumental techniques. In respect to instrument unavailability, good old bench or wet chemistry methods have been employed in this regard.

4.4.1 Bulk density determination

The bulk densities of the RMN, AMM and BMM powdered samples were determined by slowly transferring quantities of the samples into pre-weighed empty 25 mL density bottles. During the transfer of the samples, the bottles were tapped gently to ensure that the particles settled at the bottom and that void spaces were eliminated. The bulk density was calculated as the mass of sample occupying 25 mL density bottle divided by volume (25 mL).

4.4.2 Determination of the point of zero charge (pH_{pzc})

The determination of the point of zero charge was done by employing the solid addition method modified from Mall *et al.* (2006). Briefly, 50 mL of 0.01 M KNO₃ solution was introduced to a series of 100 mL titration flask with varying pH from pH 2 to pH 12. The pH adjustment was done by using 0.1 M HCl and 0.1 M NaOH

solutions. The initial pH (pH_i) was recorded and 0.1 g of *Macadamia* nutshell (RMN) were introduced to each flask containing 0.01 M KNO_3 at different pH_i . The flasks were then sealed with a rubber stopper and the mixtures were agitated for 48 h before determining the final pH (pH_f). The change in pH (ΔpH) was given by the difference between the pH_i and pH_f values. The pH_{PZC} was given by a graphical plot of ΔpH as a function of pH_i this method was followed for all pH_{PZC} determinations.

4.4.3 Determination of surface negative charge

The total negative charge on the surface of the *Macadamia* powder was determined by using a method modified from Boehm, (1994). Pholosi *et al.* (2013) stated that the ‘total’ negative charge could only be determined accurately on samples with a $\text{pH} < 3$. Subsequently, samples of RMN, AMM, BMM, 0.5 GAM, 1 GAM, 2 GAM, 0.5 GBM, 1 GBM, and 2 GBM were soaked in 0.1 M HCl to bring the pH of the materials to below pH 3. The acidified samples were filtered and dried in an oven. One and a half grams of *Macadamia* powder was transferred into separate stoppered Erlenmeyer flasks, and 25 mL of 0.10 M NaOH was added and the contents were stirred at 300 rpm for 16–20 h. The contents of the flasks were filtered under vacuum through a Whatman #4 filter paper. Thereafter, 10 mL of the filtrate was added to 15 mL of 0.10 M HCl solution in the flask. The addition of excess HCl to the filtrate was done to prevent possible adsorption of carbon dioxide at the base and was necessary since the solutions were required to stand for extended time periods before analysis (Pholosi *et al.*, 2013). Few drops of phenolphthalein indicator were added to each flask, and the solutions were titrated with 0.1 M NaOH until an endpoint was achieved. The results were expressed in mmoles H^+ neutralized by excess OH^- per gram of *Macadamia* powder.

4.4.4 Determination of extractives

RMN were dried in an oven at 105°C for 24 h then cooled in a desiccator, about 5 g of RMN labeled G_0 was introduced into a mixture of 10 mL benzene and 5 mL ethanol in a glass bottle and allowed to stand for 3 h. After the 3 h, the *Macadamia* nutshells were separated from the benzene-ethanol mixture by vacuum filtration using Whatman #4 paper. The nutshells were again dried in an oven at 105°C for 24 h, before being cooled in a desiccator. After cooling they were weighed and labeled G_1 , the extractives were calculated by using equation 4.1.

$$\%W_1 = \frac{G_0 - G_1}{G_0} \times 100 \quad 4.2$$

where the $\%W_1$ is the extractive percent weight, G_0 is the initial mass of the nutshell powder, G_1 is the final mass of the nutshell powder. This method was followed for all extractive determinations in all other materials.

4.4.5 Determination of hemicellulose

Hemicellulose was determined from the residue that was left from extractives determination of which 1 g of RMN was introduced in a flask containing 150 mL of 0.5 M NaOH solution. The mixture was refluxed at 98°C for 3 h, then the solid was separated from the mixture by a vacuum filtration through Whatman #4 paper. The *Macadamia* nutshells were rinsed with distilled water until a neutral pH. Then, the RMN was dried in an oven at 105°C for 24 h before being cooled in a desiccator, weighed and labeled G_2 . The hemicellulose was calculated by the following equation.

$$\%W_2 = \frac{G_1 - G_2}{G_0} \times 100 \quad 4.3$$

where %W₂ is the hemicellulose percent weight and G₂ is the dried mass of the hemicellulose determination. Exactly the same method was followed for all hemicellulose determination in all other materials.

4.4.6 Determination of lignin

Lignin was determined from the residue left in the hemicellulose determination, where 1 g of RMN was introduced into a flask and dried for 24 h then cooled and weighed followed by labeling it G₃. The G₃ sample was introduced into a flask and 30 mL of 72% H₂SO₄ was poured slowly into the flask. The mixture was kept between 8–15°C for 24 h and it was diluted with 300 mL of distilled water before being refluxed at 98°C for 1 h. After the mixture was cooled it was vacuum filtrated then, the RMN was rinsed with distilled water until a neutral pH. The RMN was dried for 24 h followed by cooling in a desiccator and labeled G₄. The lignin content was calculated by using equation 4.3.

$$\%W_3 = \frac{G_4(1 - W_1)}{G_3} \times 100 \quad 4.4$$

where %W₃ is the lignin percent weight, G₃ is the dried mass from hemicellulose determination (initial mass) and G₄ is the final mass.

4.4.7 Determination of cellulose

The percentage cellulose in the material was calculated using the following equation.

$$\%W_4 = 100 - (A_d + \%W_1 + \%W_2 + \%W_3) \quad 4.5$$

where %W₄ is the cellulose percent weight and A_d is the bulk density of the material (g/cm³). The same procedure was followed for other adsorbents.

4.5. Adsorption experiments for Cr(VI) removal

Adsorption studies involving raw and chemically modified *Macadamia* nutshells were conducted in a series of batch experiments. Since all the adsorption batch experiments were of similar design to the effect of pH will serve as an example to illustrate a typical experimental setup. For the effect of pH, a pH range was selected from pH 1 to pH 9. In a series of 100 mL glass bottles 0.1 g of adsorbent was added, then 25 mL of 100 mg/L adsorbate was introduced to the adsorbent in a 100 mL glass bottle and the pH was adjusted either with HCl or NaOH. The mixture was agitated for 120 min using a Multi-Channel stirrer MS-53 M from JEIO TECH (Korea, Japan) thereafter the adsorbate was separated from the adsorbent by centrifugation. The final concentration or equilibrium concentration of Cu(II), Co(II), Cd(II), and total Cr the atomic absorption spectrometer AA-7000 from Shimadzu (Kyoto, Japan) was used. For the determination of Cr(VI) the Ultra-Violet spectrometer (T80⁺, PG Instrument) was used at a wavelength of 540 nm. As a complex-forming agent 1, 5-diphenylcarbazide was used in an acidic system. The 1, 5-diphenylcarbazide reacts with Cr(VI) ions to form a Cr(III)-diphenylcarbazone complex. For other experiments, the pH was kept constant while the other parameters were varied. The range studied for the effect of time was (10–1200 min), for initial concentration it was (25–300 mg/L), for an adsorbent amount it was (0.05–0.3 g) and for temperature it was (20–40°C). This procedure was followed for the effect of different anions and only the effect of pH was studied.

4.6 Desorption or adsorbent regeneration studies

The adsorbent regeneration studies were conducted using 1 M NaOH and 1 M HCl as separate desorbing agents. Firstly adsorption of metal ions was allowed onto raw

and chemically modified *Macadamia* biosorbents for 600 min. Then, the biosorbents loaded metal ions were oven dried at 105°C and cooled to room temperature. The dry powder was placed in a glass bottle containing 20 mL of eluent and desorption time was 600 min. The sample was centrifuged and the metal concentration in the supernatant was measured. Total desorbed metal present in the solution was determined by using an AA spectrometer and UV-Vis spectrophotometer.

Chapter five

5.1 Adsorbent characterization

5.1.1 Fourier transform infrared (FTIR) spectra analysis.

Figure 5.1 shows FTIR spectra of RMN, AMM, and BMM. It is observed that all materials exhibited a similar structural backbone, implying that HCl and NaOH treatment did not completely disintegrate the structural backbone of the adsorbent. However, there were some changes in the intensity of the peaks, deformations, and shifts in wavenumbers that were observed from the treated adsorbents. The peak at $\sim 1510\text{ cm}^{-1}$ and 1603 cm^{-1} are attributed to the C=C stretching of the aromatic ring in lignin (Orton *et al.*, 2004) and are present in all three adsorbents. After the base treatment, the BMM material showed the C=O peak at 1740 cm^{-1} characteristic of aldehydes or ketones of the lignin decreases in intensity owing to NaOH modification (Orton *et al.*, 2004). Lignin deformation is seen at $\sim 1422\text{ cm}^{-1}$ spectral band. The peak at 1456 cm^{-1} is attributed to the C-H bending of a methyl group from lignin. The presence of the in-plane CH bending at $\sim 1373\text{ cm}^{-1}$ was attributed to the hemicellulose or cellulose (Felix and Gatenholm, 1991). The peak shows a decrease in intensity in the order $\text{RMN} > \text{AMM} > \text{BMM}$ suggesting that NaOH extracted more hemicellulose.

A similar observation is made in the region of 2926 to 2855 cm^{-1} attributed to the loss of aliphatic compounds following NaOH treatment. The peaks at 1652 and 1605 cm^{-1} representing a carbonyl group C=O stretch and a primary amine N-H band respectively merged to form a band at 1604 cm^{-1} for BMM adsorbent representing amine groups, suggesting that NaOH extracted more carbonyl groups than amine groups. The spectra for the AMM material shows a similar merging of

peaks at 1652 and 1605 cm^{-1} but the difference is that instead of forming a peak representing amine groups, the peak formed at 1641 cm^{-1} represented a carbonyl group. The presence of a carbonyl group at 1641 cm^{-1} indicates that the HCl was able to extract or react with amine groups than the NaOH. The modification of RMN by NaOH and HCl resulted in different changes taking place on the adsorbent surface due to acid-base interactions between the adsorbent and extracting solutions. The prominent decrease in the intensity of the peak at 3338 cm^{-1} representing O–H group from cellulose or hemicellulose for the RMN material, was attributed to the extraction of cellulose and hemicellulose compounds by HCl (Zhao *et al.*, 2013).

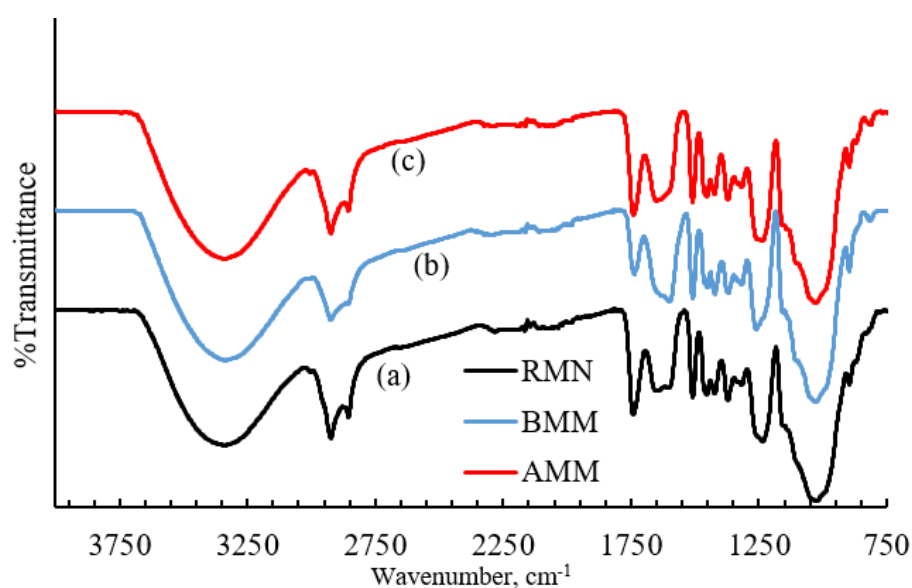


Figure 5.1: FTIR spectra of RMN (a), BMM (b), and AMM (c) adsorbents

Figure 5.2 presents FTIR spectra of AMM (a), 0.5 GAM (b), 1 GAM (c) and 2 GAM (d) adsorbents. The broadband at about 3330 cm^{-1} which is a characteristic of bonded OH functional groups is observed to split into two peaks in the grafted material. This splitting phenomenon is attributed to the addition of carboxylic group from acrylic acid. The peak at 1643 cm^{-1} attributed to C=O stretch of the

carboxylic group also split into two peaks, 1659 and 1594 cm^{-1} representing C=O stretch of carboxylic group and N–H bend for primary amine. The appearance of an amine peak can be attributed to the exposure of amine groups which could have been hindered by the presence of cellulose or hemicellulose that were extracted by the acrylic acid during grafting. Another splitting was observed for the peak at $\sim 1243 \text{ cm}^{-1}$ attributed to C–N stretch of aromatic amines. The new peaks representing C–N stretch and C–O stretch for the carboxylic acid group, were formed at 1260 and 1232 cm^{-1} , respectively. The disappearance of the peak at 2855 cm^{-1} for C–H stretch was attributed to the extraction of lignocellulosic compounds from the AMM material due to acrylic grafting. All the notable changes in surface properties of the AMM material after grafting proved that indeed functionalization did take place.

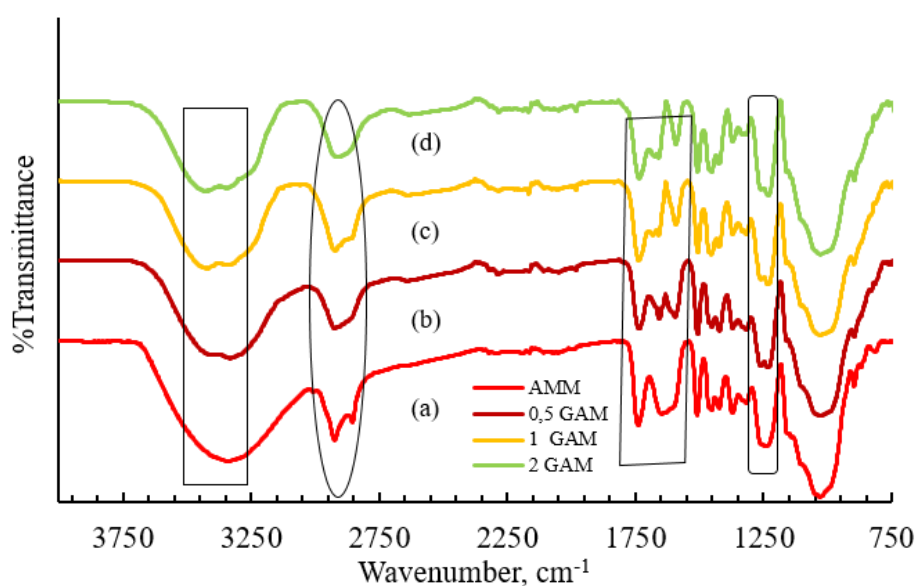


Figure 5.2: FTIR spectra of AMM (a), 0.5 GAM (b), 1 GAM (c) and 2 GAM (d) adsorbents.

Figure 5.3 shows the FTIR spectra of BMM and its grafted derivatives, 0.5 GBM, 1 GBM, and 2 GBM. The acrylic acid grafting affected the surface of the BMM

material in a similar way to that of the AMM material represented in Figure 5.2. The splits and disappearance of peaks were similar but occurred at different wavenumbers. The peak at 1740 cm^{-1} for the RMN decreased in intensity following base modification. However, after grafting the BMM material that has been grafted with acrylic acid the peak at 1739 cm^{-1} increased in intensity. The increase was attributed to the addition of carboxylic functional groups owing to acrylic acid grafting. No notable change was observed as a result of using different concentrations of acrylic acid. That is 0.5 GBM, 1 GBM, and 2 GBM all displayed similar FTIR spectral features.

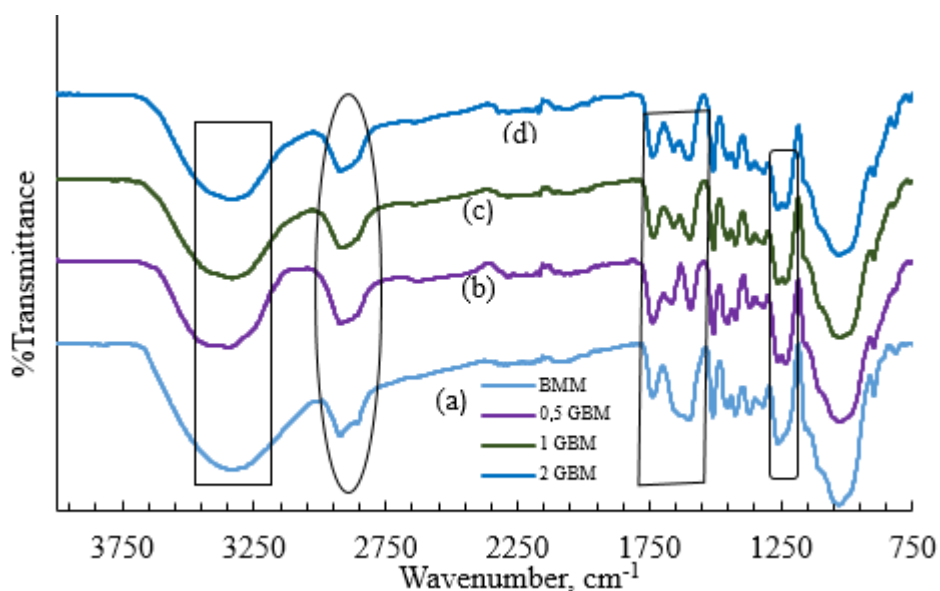


Figure 5.3: FTIR spectra of BMM (a), 0.5 GBM (b), 1 GBM (c), and 2 GBM (d) adsorbents.

5.1.2 Component and elemental analysis

Agricultural waste materials have surface compounds that characteristically comprise of cross-linked polymeric compounds such as lignin, cellulose, and hemicellulose (Saini *et al.*, 2015). *Macadamia* nutshells are one such material. Table 5.1 shows the percentage surface components demonstrated by lignin,

cellulose, and hemicellulose as well as the elemental composition of carbon, hydrogen, nitrogen, oxygen and oxygen/carbon ratio (atomic) for RMN, AMM, BMM, 0.5 GAM, 1 GAM, 2 GAM, 0.5 GBM, 1 GBM and 2 GBM. The percentage of oxygen was calculated by difference, that is, the sum of %C, %H, and %N was subtracted from 100% to get %O.

The elemental analysis of all the adsorbents showed that all the materials had a carbon percentage that was approximately 50%, indicating that the adsorbents consist mainly of carbon on their surface and this was typical of biosorbents. The nitrogen content of the BMM decreased significantly while that of the AMM increased slightly following base and acid modification of the RMN. This could be that the HCl, NaOH and acrylic acid used for treatment had a slight effect on the extraction of nitrogen compounds. The BMM material had an increase in the oxygen content compared to the AMM material. All the acrylic grafted materials had an increased content of oxygen, the increase in oxygen content can be attributed to the treatment of NaOH and acrylic acid of which they both carry oxygen that may have attached to the surface of the materials.

The hydrogen content was significantly similar for the grafted materials, the similarity can be attributed to the equal concentrations of acrylic acid which were 0.5, 1 and 2 M used for grafting. The BMM material has a hydrogen percentage of 5.71% the lowest of all the materials and that could be credited to extraction by NaOH. The O/C ratio was lowest for the AMM material, the implication of this may be that the HCl used for modification had a high affinity for oxygen-containing groups. This was proven by the lower cellulose content of 29.54% for AMM material compared to 40.64% for the BMM material.

Table 5.1: Surface compounds and elemental analysis for RMN, AMM, BMM, 0.5 GAM, 1 GAM, 2 GAM, 0.5 GBM, 1 GBM, and 2 GBM.

Adsorbents	Elemental analysis							
	Cellulose %	Hemicellulose %	Lignin %	Carbon %	Hydrogen %	Nitrogen %	Oxygen* %	O/C
RMN	34.48	21.48	11.91	50.56	5.94	0.51	42.99	0.850
AMM	29.54	24.31	31.90	51.34	5.92	0.54	42.20	0.822
BMM	40.64	17.47	31.68	51.24	5.11	0.34	43.11	0.841
0.5 GAM	-	-	-	50.27	5.81	0.52	43.40	0.863
1 GAM	-	-	-	51.36	5.74	0.52	42.38	0.825
2 GAM	-	-	-	49.71	5.85	0.52	43.92	0.884
0.5 GBM	-	-	-	50.27	5.81	0.52	43.40	0.863
1 GBM	-	-	-	48.88	5.82	0.49	45.79	0.937
2 GBM	-	-	-	49.76	5.85	0.51	43.88	0.882

* Computed by difference.

It can be observed that the amount of cellulose (34.48%) in the RMN material decreased after treatment with HCl (29.54%) while it increased to 40.64% following NaOH treatment. An opposite trend was observed in the amount of hemicellulose. In this case, the percentage hemicellulose in RMN material (24.31%) increased after acid treatment while it decreased (17.47%) after base treatment. The amount of lignin increased equally following both acid and base treatments. The observed differences can be attributed to the compatibility of HCl and NaOH to the extraction of cellulose and hemicellulose, respectively. Cellulose is more acid soluble thus highest extraction with HCl, whereas hemicellulose is more base soluble. The increase in cellulose following base treatment could be attributed to hydrolysis of esters leading to the production of more alcohol functional groups on the surface of BMM material. This can be further supported by the higher oxygen content observed on the BMM material compared to RMN and AMM materials.

The differences in the percentages of the cellulose, hemicellulose, and lignin content of the RMN material related to the BMM and AMM materials demonstrated that chemical treatment resulted in the chemical change of the treated materials. The components analysis of *Macadamia* nutshells is comparable to other adsorbents that are based on agricultural waste such as legume straw and apricot stone (Li *et al.*, 2004). It was reported that the legume straw exhibited 28.13% cellulose, 34.08% hemicellulose, and 34.03% lignin and the apricot stone exhibited 22.36% cellulose, 20.83% hemicellulose and 51.43% lignin. The difference in surface components of the two adsorbents was attributed to the presence of more CO and CO₂ for legume as a circumstance of higher cellulose and hemicellulose content.

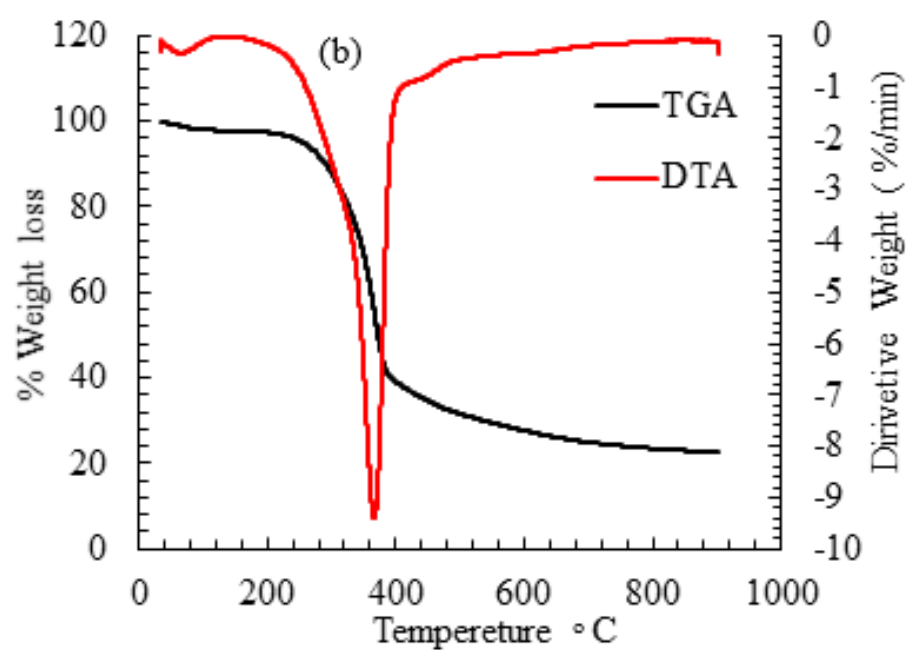
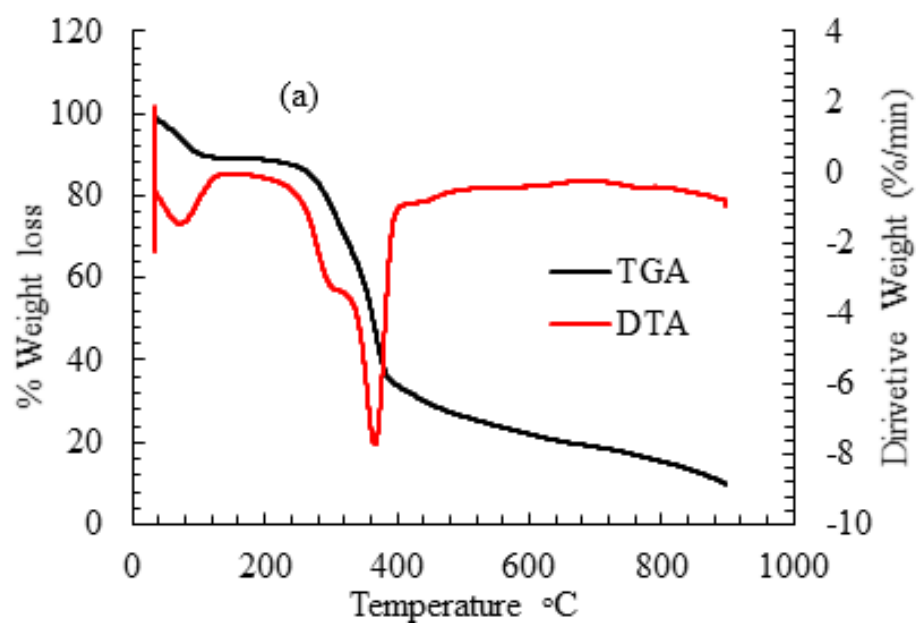
5.1.3 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

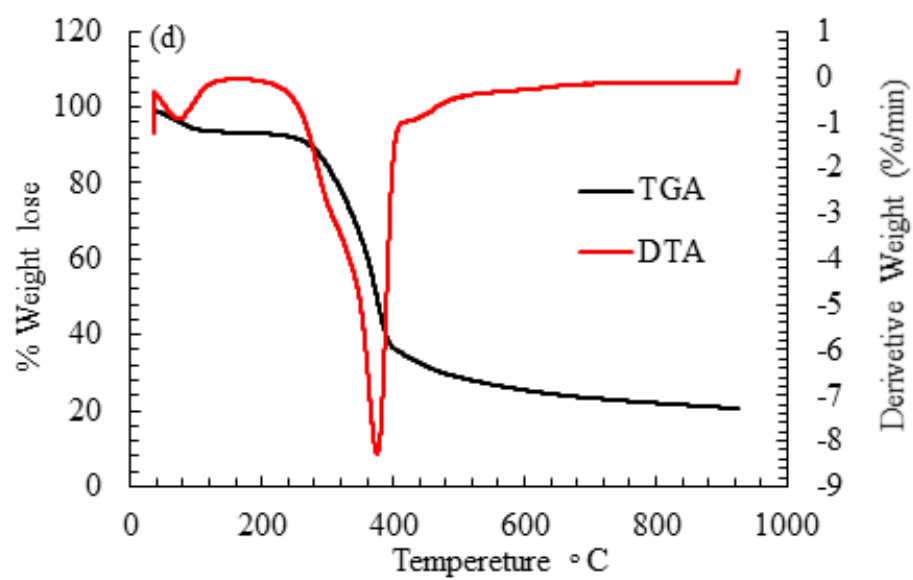
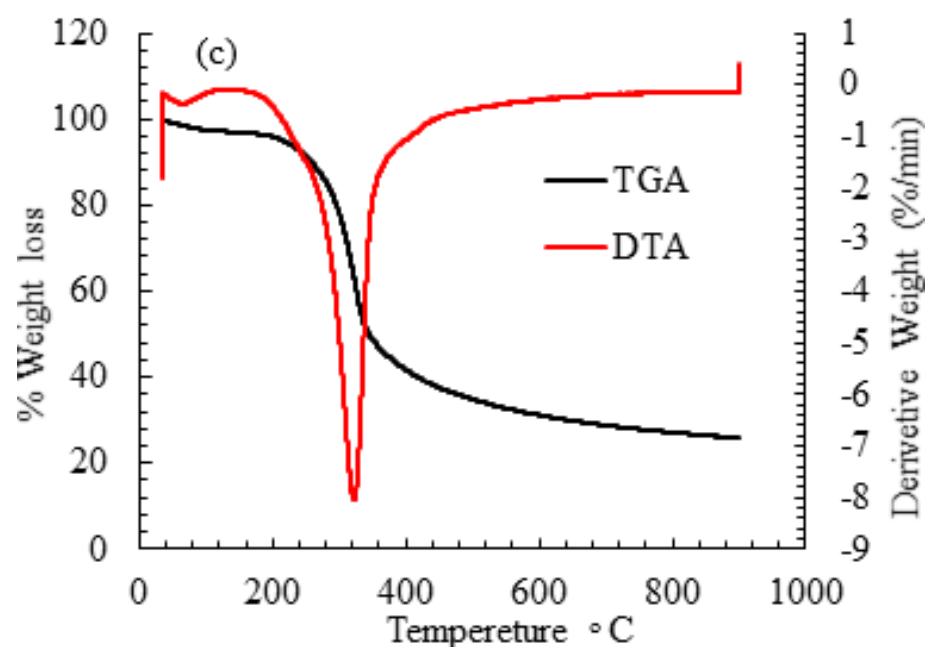
Figure 5.4 (a–e) represents the TGA and DTA thermograms of RMN, AMM, BMM, 0.5 GAM and 0.5 GBM adsorbents. The RMN, 0.5 GAM and 0.5 GBM thermograms exhibited four decomposition stages while the AMM and BMM showed only three decomposition stages. The first decomposition observed at about 120°C was attributed to dehydration of adsorbed water. The second stage from 120°C to 310°C was characterized as representing hemicellulose degradation and loss of volatile substances such as CH₄, H₂, CO₂, and CO (Rangabhashiyam and Selvaraju, 2015). The third stage occurring around 310°C to 380°C was attributed to the degradation of cellulose and the last stage is the degradation of lignin (Li *et al.*, 2004). After the RMN adsorbent underwent HCl and NaOH treatment, its thermal stability and chemical composition were affected. Firstly the residual weight losses for the AMM and BMM adsorbents were 22.45% and 25.70%, respectively, which was an increase compared to 10.25% for RMN.

Secondly, the shoulder present at around 120°C to 310°C for the RMN was missing from both the AMM and BMM adsorbents. This implied that the HCl and NaOH treatment extracted more of hemicellulose and volatile compounds from RMN material. It was also shown in Table 5.1 that the RMN lost more hemicellulose after chemical modification with HCl and NaOH. The remaining hemicellulose contents were at 24.31% and 17.37% for AMM and BMM, respectively. The dehydration stage for the AMM and BMM adsorbents quantified to 2% and 3% weight loss percentage was much lower compared to the 12% for the RMN. This can be accounted for in two ways: The first would be that the AMM and BMM adsorbents underwent two cycles

of drying before chemical modification and after. The second could be attributed to the loss of hemicellulose resulting in loss of association with water molecules due to the absence or lack of hydroxyl groups on the AMM and BMM materials (Pakade *et al.*, 2016). Generally, because the hydrophilic components of plant material can be linked to the amount of adsorbed water and those components get extracted by the acid and the base resulting in a low percentage of dehydration for AMM and BMM (Shalwan and Yousif, 2013). Figure 5.4 (d, e) shows the reappearance of the shoulder peak at $\sim 310^{\circ}\text{C}$. This reappearance can be attributed to the presence of volatile components such as H_2 , CO_2 , CO , and CH_4 that are reintroduced by the grafting with acrylic acid.

Dubinsky *et al.* (2004) studied the thermal degradation of poly (acrylic acid) containing copper nitrate. The shoulder around 142°C to 335°C was attributed to the loss of CO_2 , CH_4 , and acrylic acid monomer. The similarities of the shoulder region to that of the current study validated that indeed acrylic acid was grafted on the AMM and BMM adsorbents. Acrylic acid grafting was also substantiated by the increase in the oxygen content of the grafted adsorbents depicted in Table 5.1.





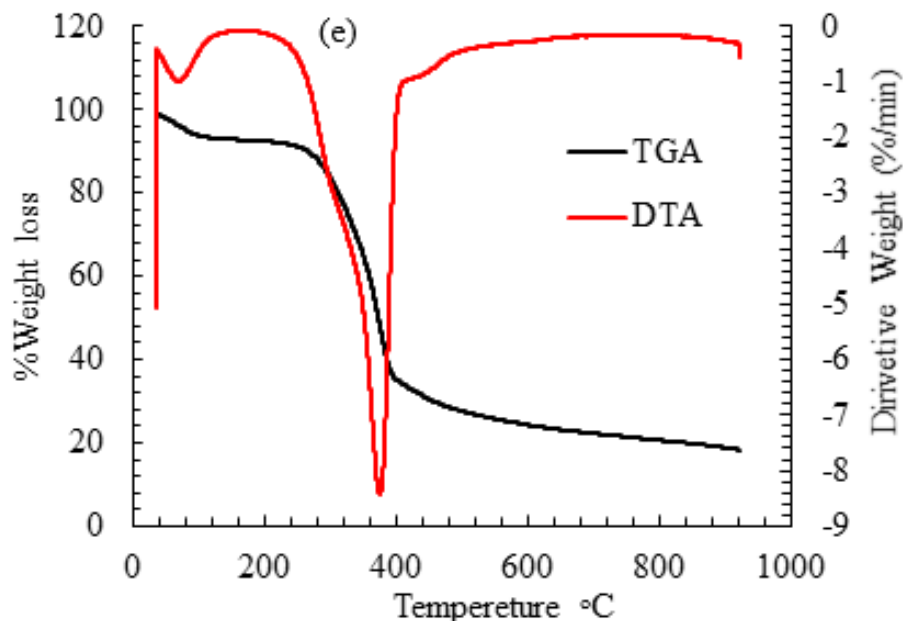


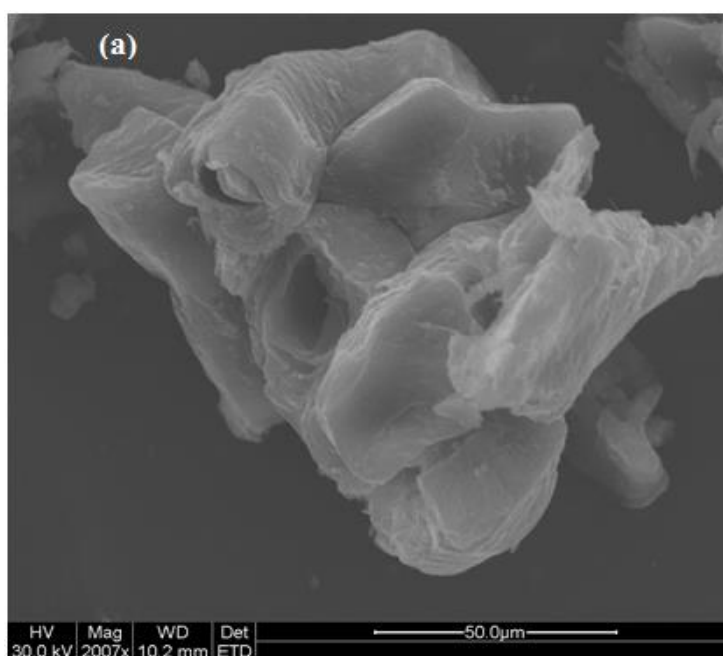
Figure 5.4: TGA and DTA thermograms for RMN (a), AMM (b), BMM (c), 0.5 GAM (d), and 0.5 GBM (e) adsorbents.

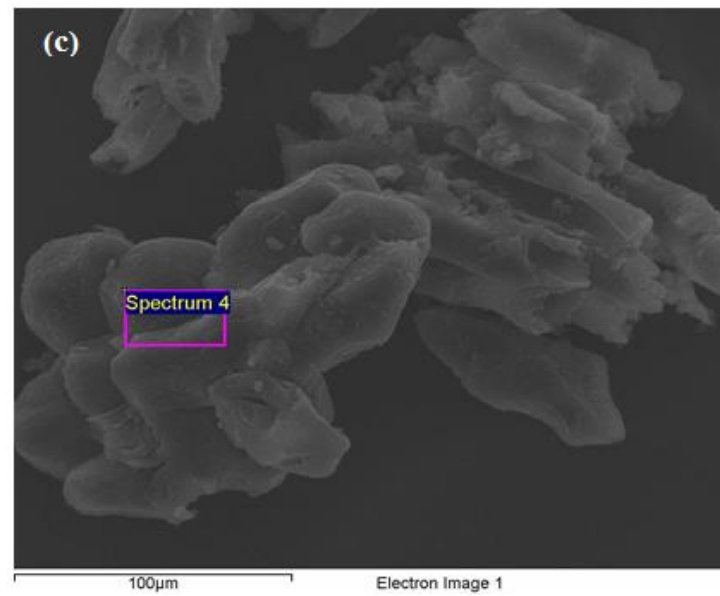
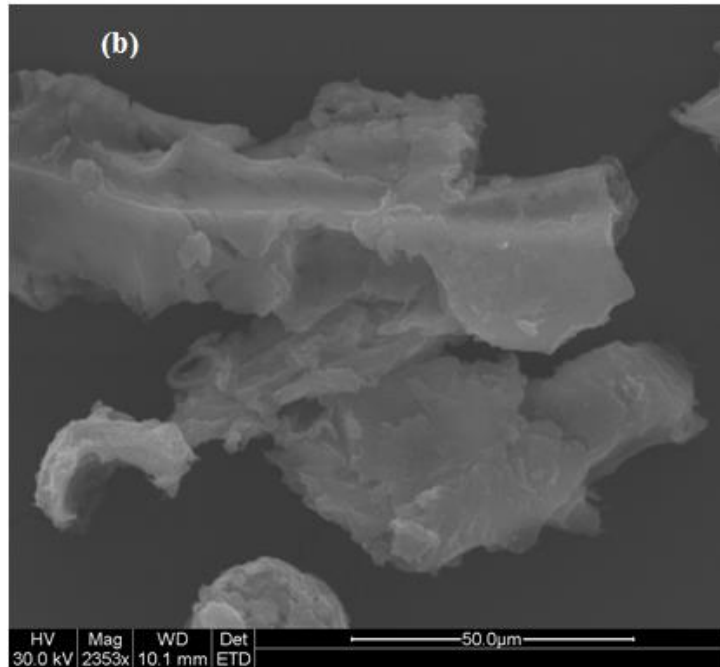
5.1.4 Scanning electron microscopy (SEM) analysis

The SEM images in Figure 5.5 (a–e) depicts the RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM surface morphological properties of *Macadamia* Nutshells. The image depicted in Figure 5.5 (a) for RMN shows bulk particles stacked against each other having halo spherical openings. Around the spherical opening, it appears as multilayered material folded one onto another. The opening can serve as pores and provide a pathway for adsorption of metal ions (Ansari *et al.*, 2016). The material had a laminar surface with wrinkles and smaller abrasive layers. This is consistent with the surface composition of *Macadamia* nutshells that have been determined to be consisting of cross-linked cellulose, hemicellulose, and lignin as shown in Table 5.1. Figure 5.5 (b) shows a SEM image of AMM. It can be said that the acid treatment

relatively affected the surface morphology of the RMN material. The AMM material showed to contain fewer wrinkles on its surface due to modification.

The effect of base treatment on the surface of RMN is depicted in Figure 5.5 (c). The BMM material had a similar surface morphology to that of the RMN and AMM material. The chemical treatment may remove acid or base soluble compounds but their removal did not adversely affect the surface morphology.





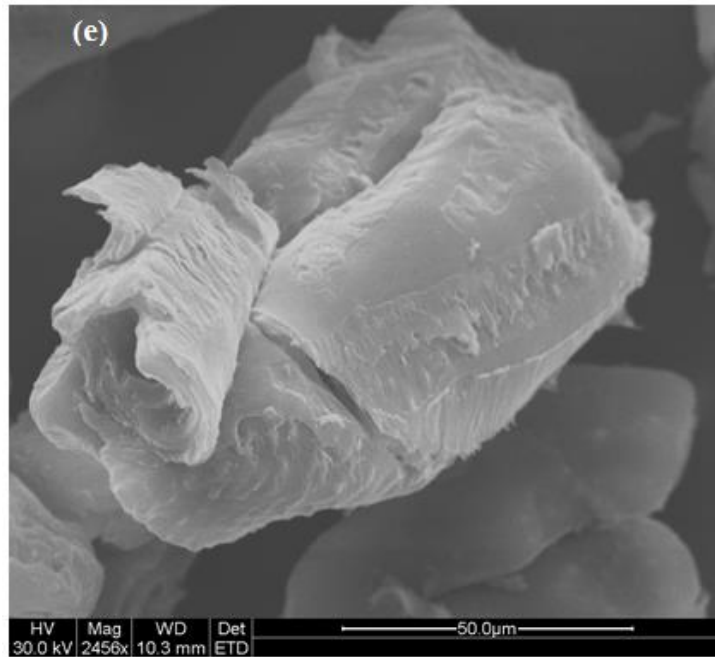
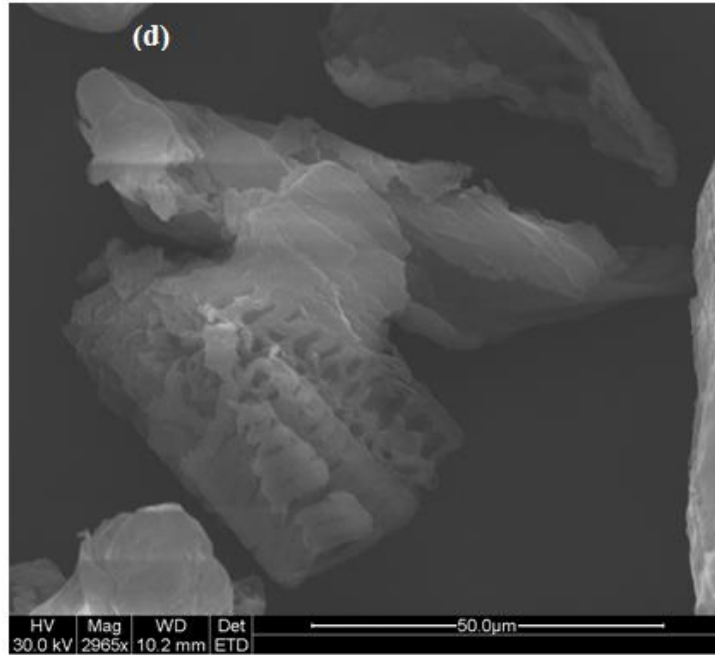


Figure 5.5: SEM image for RMN (a), AMM (b), BMM (c), 0.5 GAM (d), and 0.5 GBM (e)

Figure 5.5 (d, e) shows SEM images of the 0.5 GAM and 0.5 GBM materials respectively. The notable difference to the RMN, AMM, and BMM surface

morphology was that the grafted material had slightly lower rough edges (Ensuncho-Muñoz and Carriazo, 2015). Comparing SEM images of the current study with other researchers, it was noted that the surface morphology of agricultural waste material is different from one material another and have pores of different sizes. Bagasse ash was reported to have a smooth surface (Aigbodion *et al.*, 2010) whilst rice husk was reported to have a rough surface (Ensuncho-Muñoz and Carriazo, 2015).

5.1.5 Powder X-ray diffraction (PXRD) analysis

Figure 5.6 (a–c) depicts XRD patterns for RMN, AMM, and BMM adsorbents. The patterns showed a difference in the intensities, attributed to the extraction of organic groups from the RMN due to HCl and NaOH treatment. The XRD patterns displayed similarities with those reported by Bereman *et al.* (1979). The adsorbents were made up a monoclinic morphological symmetry, having a probable space group that is centrosymmetric. The peaks at $2\Theta=22.14^\circ$ and 44.06° can be attributed to the turbostratic structure of microcrystals that resembles the presence of graphite particles Drewniak *et al.* (2015). The mixture of broad and the sharp peaks can be ascribed to the morphological combination of amorphous and crystalline nature of the adsorbents, respectively (Kumar *et al.*, 1997). The peak at $2\Theta=22.14^\circ$ shifted to the left for the BMM and to the right for the AMM an indication that the acid and the base treatment affected the RMN material differently. This was also seen by the different percentages of lignin, cellulose, and hemicellulose displayed in Table 5.1.

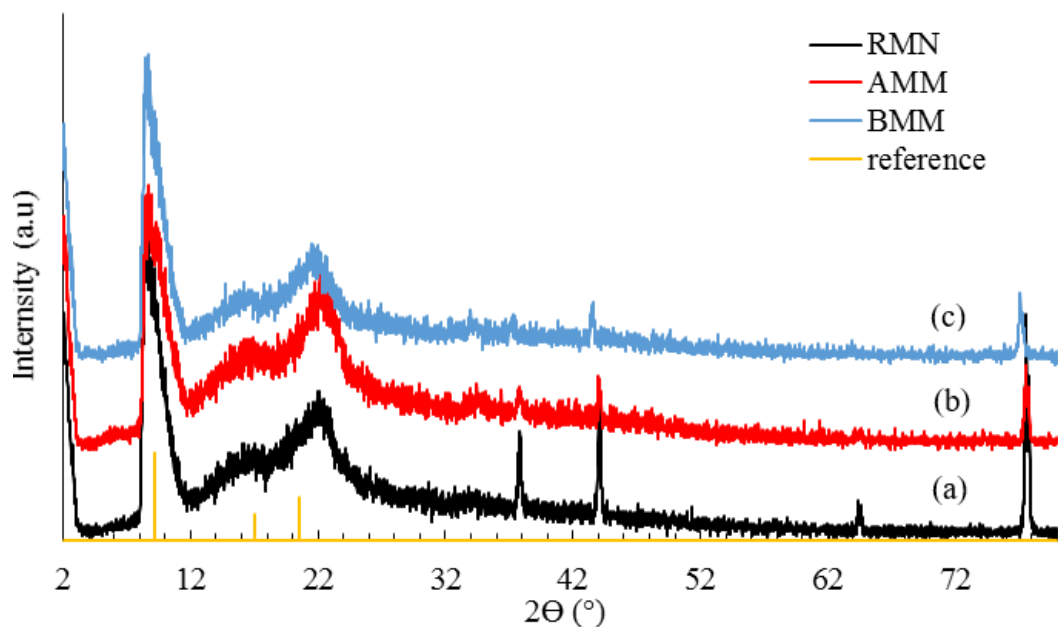


Figure 5.6: XRD patterns for the RMN (a), AMM (b), and BMM (c) adsorbents.

The XRD patterns showing the effects of grafting on AMM material are displayed in Figure 5.7 (a–b). After the AMM adsorbent was grafted with acrylic acid the peak below $2\theta=10^\circ$ disappeared. This was attributed to the extraction of acrylic acid soluble compounds during grafting. Other notable differences were peak broadness, intensities and sharpness.

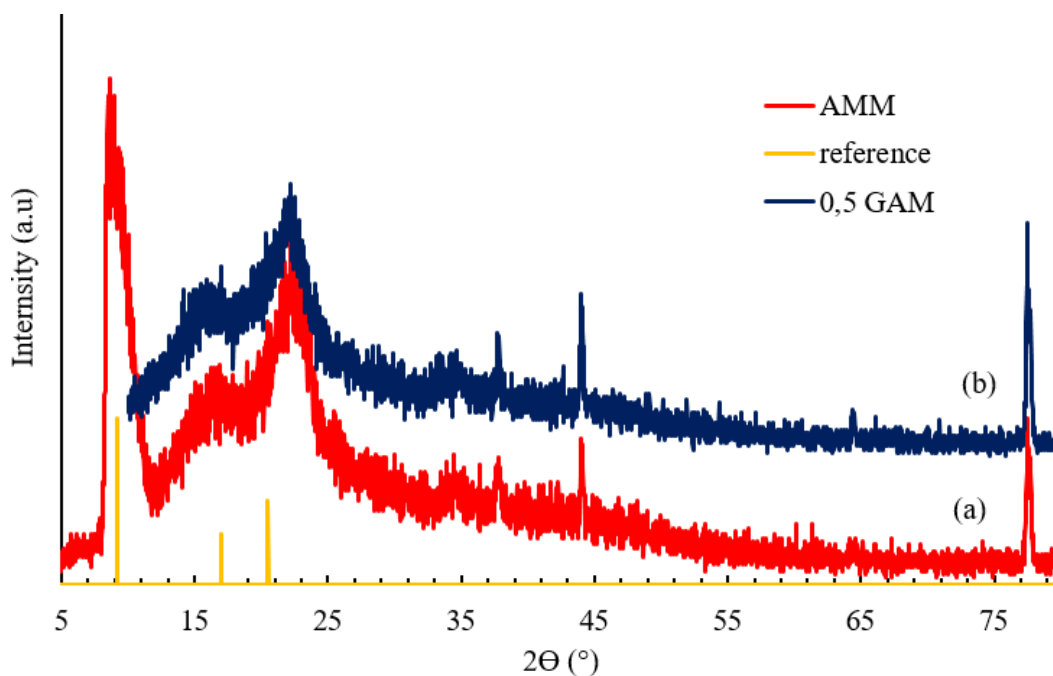


Figure 5.7: XRD patterns of AMM (a) and 0.5 GAM (b) adsorbents, effects of acrylic acid grafting.

Figure 5.8 displays the XRD patterns for BMM and 0.5 GBM adsorbents. A similar pattern which showed the disappearance of the peak at $2\theta=10^\circ$ was observed again. A reappearance of the peak at $2\theta=36^\circ$ was observed for the 0.5 GBM material and a similar observation was made in the TGA analysis where a shoulder peak attributed to volatile matter or hemicellulose reappeared. This reappearance of peaks confirmed structural changes due to chemical modification as also was observed in the FTIR spectra shown in Figure 5.2.

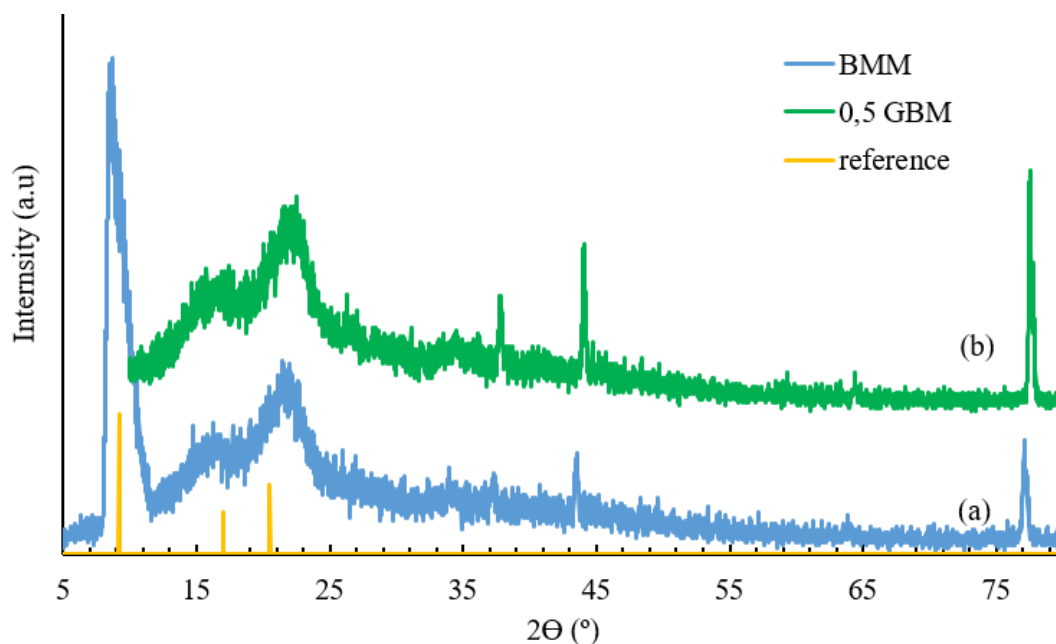


Figure 5.8: XRD patterns of BMM (a) and 0.5 GBM (b) adsorbents, the effect of acrylic acid grafting.

The XRD patterns for the RMN, AMM, and BMM adsorbents after the adsorption of Cr(VI) are shown in Figure 5.9. These XRD patterns displayed similar characteristics to those observed in Figure 5.7 (b) and 5.8 (b) for 0.5 GAM and 0.5 GBM. The peak at $2\theta=10^\circ$ disappeared in all the materials loaded with Cr. Since during adsorption of Cr(VI) acidic conditions are used and for grafting an acid was also used. Thus, accounting for the peak disappearance when the adsorbent underwent acid treatment during adsorption and grafting process. Acid and base treatment followed by grafting has proven to be an effective method not only to change the surface characteristics of the adsorbent but also to prevent leaching of organic compounds for an effective adsorbent.

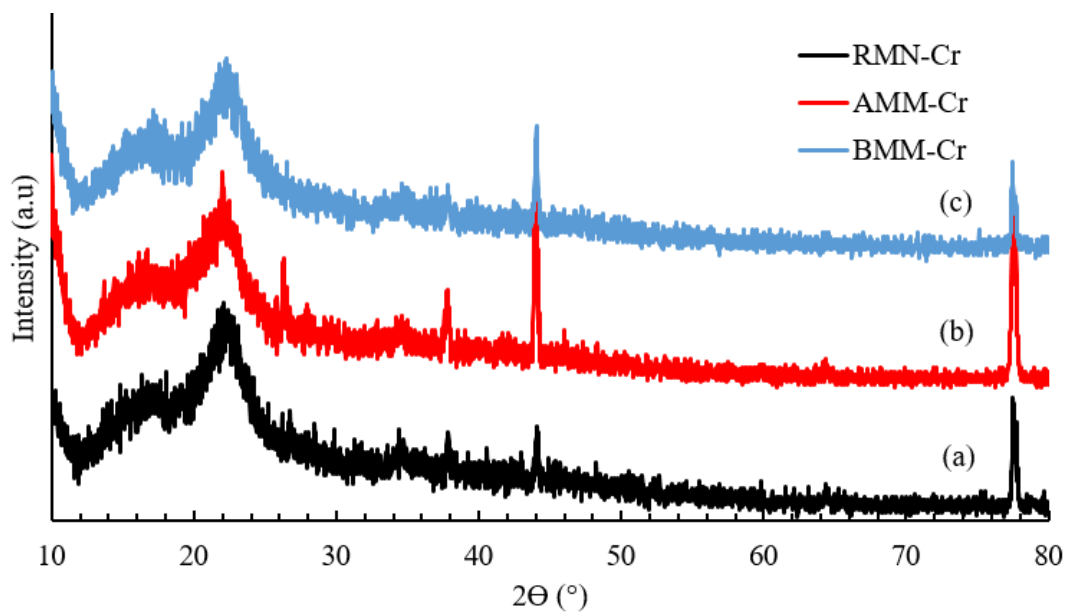


Figure 5.9: XRD patterns for RMN (a), AMM (b), and BMM (c) after the adsorption of Cr(VI)

5.1.6 Bulk density determination

The bulk densities of RMN, AMM, BMM, 0.5 GAM, 0.5 GBM, 1 GAM, 1 GBM, 2 GAM, and 2 GBM are presented in Table 5.2. The determination of bulk density of a material gives an indication of how much void spaces are present in a material as bulk density is inversely proportional to the number of void spaces. Treatment of RMN with HCl and NaOH lead to the extraction of plant components and created void channels in the matrix of the material.

Table 5.2: showing bulk density, surface negative charge, the point of zero charge, and BET surface area.

Adsorbent	Bulk density (g/mL)	Surface charge (mmol/g)	pHpzc	BET (m ² /g)
RMN	0,612	2,39	5,96	0,018
AMM	0,582	2,35	6,30	0,065
BMM	0,574	6,67	6,62	0,546
0.5 GAM	0,537	2,11	6,76	*
1 GAM	*	2,21	6,85	*
2 GAM	*	2,13	6,88	*
0,5 GBM	0,552	4,46	6,42	*
1 GBM	*	4,22	6,52	*
2 GBM	*	4,44	6,61	*

*Data not acquired

After the modification with HCl and NaOH, the bulk density of RMN decreased from 0.612 g/mL to 0.584 and 0.574 g/mL for AMM and BMM, respectively. The decrease in bulk density was attributed to the release of some plate components during treatment. The percentage decrease in bulk density after treatment with NaOH and HCl was 6.2 and 4.6% for BMM and AMM respectively. This showed that *Macadamia* nutshells contained components that had a higher affinity for base extraction. As TGA results showed, this fraction that was attributed to the presence of hemicellulose fraction. Much higher percentage decrease of 31.0, 36.4 and 60.1% in bulk density were reported when corn cob, soybean hull, and almond hull were respectively treated with 0.1 M NaOH for 1 h (Wartelle and Marshall, 2000). The lower values obtained with *Macadamia* nutshells could be due to inefficient extraction process or that *Macadamia* nutshells do not contain a high percentage of extractives that could be

removed by either acid or basic treatment. A further decrease in bulk density was observed in the acrylic grafted materials following grafting, largely because of removal of some components during grafting with acrylic acid.

5.1.7 Surface negative charge determination

The surface negative charge of an adsorbent gives an indication about the density of negatively charged organic functional groups present on the surface (Ofomaja *et al.*, 2010). The presence of organic functional groups on the surface of an adsorbent act as metal ion chelators. The surface negative charge of RMN, AMM, BMM, 0.5 GAM, 0.5 GBM, 1 GAM, 1 GBM, 2 GAM and 2 GBM adsorbents is displayed in Table 5.2. The RMN has a surface charge of 2.39 mmol/g which was higher than that of soybeans hull 1.33 mmol/g reported by Marshall *et al.* (1999) but lower than that reported by Pholosi *et al.* (2013) for pine cone powder 3.82 mmol/g. This demonstrates the diverse functionalities of agro-based biosorbents. The HCl modification of RMN did not affect the surface charge greatly having 2.35 mmol/g for AMM material. However, the NaOH modification resulted in a significant increase in surface charge at 6.67 mmol/g. The increase was attributed to the formation of ionic groups during hydrolysis by NaOH. In contrast, the grafting of acrylic acid on the BMM and AMM adsorbents resulted in a decreased surface negative charge for the grafted materials as opposed to the increase expected, due to the presence of anions. The anomaly was not explored further.

The BET surface area for RMN, AMM, and BMM was 0.018, 0.065, and 0.546 m²/g, respectively. After the acid and base modification of RMN, the surface area increased in this order BMM > AMM > RMN with the BMM adsorbent having the highest

surface area. The surface area trend is comparable with the bulk density trend which decreased in this order $BMM < AMM < RMN$ shown in Table 5.1. The surface area of RMN, AMM, and BMM obtained in this study was comparable to that of rice husk $1.12 \text{ m}^2/\text{g}$ and saw dust $1.16 \text{ m}^2/\text{g}$ respectively reported by Bansal, Singh and Garg, (2009).

5.1.8 Point of zero charge (pH_{PZC})

The point of zero charge (pH_{PZC}) of an adsorbent is described as the pH value point where the surface charge of an adsorbent is zero or neutral. That is, the charge of the positive and negative surface sites are equivalent (Fiol and Villaescusa, 2009). Below the pH of the point of zero charge (pH_{PZC}), the surface of the adsorbent is said to be more positive and above the (pH_{PZC}) the surface is more negative. The pH_{PZC} for RMN, AMM, BMM, 0.5 GAM, 0.5 GBM, 1 GAM, 1 GBM, 2 GAM, and 2 GBM adsorbents is shown in Table 5.2. The pH_{PZC} value for the RMN material was 5.96 and it increased in all other materials following functionalization. This implied that the functionalized materials assumed a much more basic character after treatment as was observed by Ofomaja *et al.* (2009) after treatment of pine cone with organic solvents. When comparing the pH_{PZC} of pine cone (pH_{PZC} 7.49) and RMN it can be concluded that the RMN (pH_{PZC} 5.96) had more acidic groups than basic groups. The BMM had a higher pH_{PZC} 6.62 indicating that more acid functional groups were extracted by the NaOH.

The pH_{PZC} of the grafted acid materials (0.5 GAM, 1 GAM, and 2 GAM) increased compared to the AMM while that of the grafted base materials (0.5 GBM, 1 GBM, and 2 GBM) decreased compared to the BMM. The pH_{PZC} of the grafted base materials decreased due to added negativity imparted by the carboxylate ions from the acrylic

acid. On the other hand, the increased pH_{PZC} displayed by the grafting acid materials implied a gain in positivity.

5.2 Adsorption of selected trace metals

5.2.1. The effect of solution pH on Cd(II) adsorption

The effect of the solution pH on the removal of Cd(II) ions from aqueous solution by RMN, AMM, and BMM biosorbents was studied at a pH range of 2 to 8 and the results are illustrated in Figure 5.10. It can be observed that as the pH was increased from pH 2 to pH 7 more removal of Cd(II) ions was achieved for all the materials with the BMM material having the highest percent removal. From pH 7 to pH 8 the percent removal of Cd(II) decreased slightly. It was noted that all the materials exhibited poor removal efficiency for Cd(II) of less than 25% in the entire pH range studied. The pH of the solution does not merely affect the trace metal speciation but also the nature of the adsorbent.

Under acidic conditions, the surface of the adsorbent may become protonated and the most dominant cadmium species are Cd^{2+} and $Cd(OH)^+$ (Weerasooriya and Priyadharshane, 1999) thus, leading to low removal of cadmium. The adsorbent surface is mainly positively charged and the cadmium species are also positively charged resulting in electrostatic repulsion. Under basic conditions, the surface of the adsorbent may be deprotonated and the cadmium species starts precipitating. Meaning that as parts of the Cd(II) get adsorbed another part gets precipitate thus, leading to higher removal percentage as the pH was increased. Another contributing factor is the pH_{PZC} of the RMN, AMM and BMM material is 5.96, 6.62 and 6.30, respectively as

depicted in Table 5.2. At pH levels above the aforementioned pH_{PZC} values, the surface of the respective adsorbents became deprotonated resulting in electrostatic attraction between the adsorbent surface and the cadmium species. This trend has been observed by a number of researchers (Garg *et al.*, 2008; Ammari, 2014; Iqbal *et al.*, 2016). Thus, the removal of cadmium increased with increasing pH levels due to electrostatic attraction between positively charged cadmium species and the negatively charged adsorbent surface (Cheraghi, Ameri and Moheb, 2015).

Earlier Kumar and Bandyopadhyay (2006) reported the use of NaOH modified rice husk for the removal of Cd(II) ions from aqueous solution. The reported effect of pH trend was similar to the one reported in this study, where the removal of Cd(II) ions increased with increasing pH. The increase was attributed to the decrease concentration of H^+ ions as the solution became less acidic, resulting in an increased removal of Cd(II) ions. This is because the H^+ ions compete with the Cd(II) ions for the available adsorption sites at lower pH resulting in a lower removal of Cd(II) ions. The decrease in percent removal beyond pH 7 attributed to the formation of soluble hydroxyl complexes of $\text{Cd}(\text{OH})_2$ (Cheraghi *et al.*, 2015).

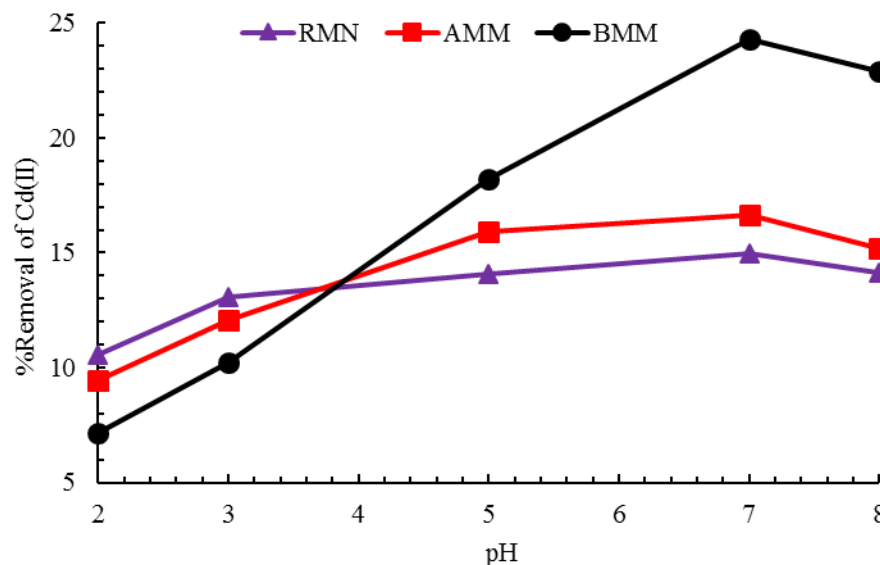


Figure 5.10: The effect of solution pH on the adsorption of Cd(II) ions by RMN, AMM, and BMM. Adsorption conditions (contact time 120 min, initial concentration 100 mg/L, mass of adsorbent 0.1 g and sample volume 20 mL)

5.2.2 The effect of solution pH on Co(II) adsorption

Figure 5.11 illustrates the effect of solution pH on the adsorption of Co(II) ions from aqueous solution by RMN, AMM, and BMM materials at a pH range of 2 to 8. It can be observed that the increase in the solution pH resulted in an increase in the percent removal of Co(II) for all materials with the BMM material having the highest % removal at pH 7 and pH 8 for the RMN and AMM adsorbents. Similar to Cd(II) removal, all removal percentages were less than 25% and same trend of $RMN < AMM < BMM$ for efficiency was observed.

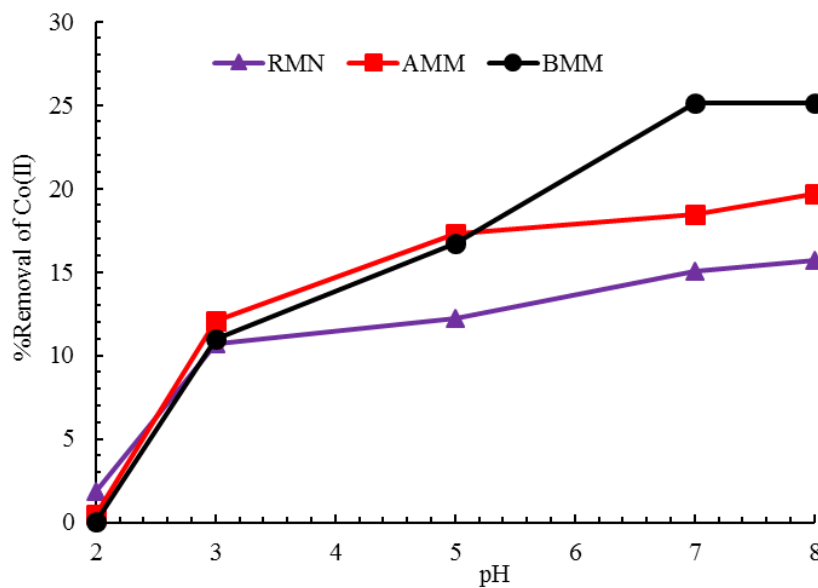


Figure 5.11: The effect of pH on the adsorption of Co(II) ion from aqueous solutions by RMN, AMM, and BMM materials. Adsorption conditions (contact time 120 min, initial concentration of Co(II) ions 100 mg/L, 0.1 g adsorbent mass and sample volume 20 mL).

The protonation–deprotonation phenomenon together with the pH_{PZC} explained in the Cd(II) removal also apply here. Abbas *et al.* (2014) also observed an increase in the removal of Co(II) with the increase in pH and the higher removal at higher pH was attributed to the electrostatic attraction between adsorbent and adsorbate due to the decreased number of positively charged adsorption sites.

5.2.3 The effect of solution pH on Cu(II) adsorption

Figure 5.12 depicts the effect of pH on the adsorption of Cu(II) ions from aqueous solutions at a pH range of 2 to 8, using the RMN, AMM, and BMM biosorbents.

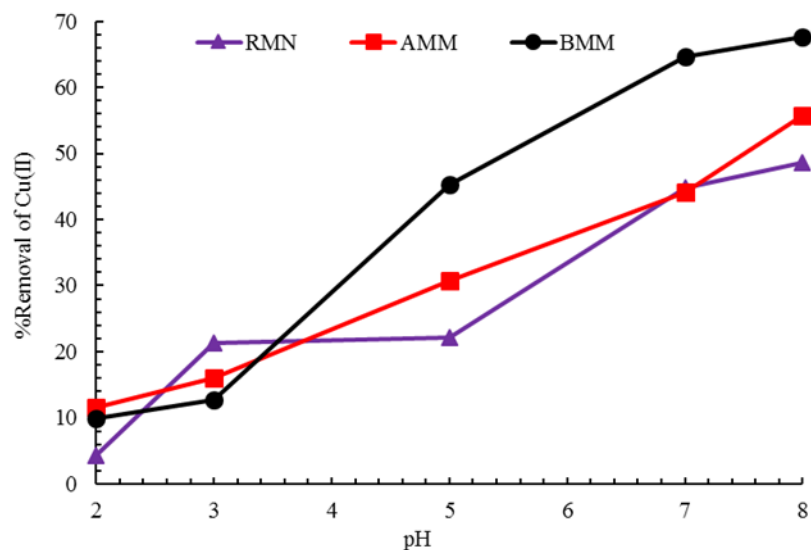


Figure 5.12: The effect of solution pH on the adsorption of Cu(II) ion by RMN, AMM, and BMM. Adsorption conditions (contact time 120 min, initial concentration 100 mg/L, adsorbent mass 0.1 g and sample volume 20 mL).

The percent removal of Cu(II) ion increased with increasing pH. High percent removal of Cu(II) ion was achieved at higher pH for all the materials. This trend was similar to the one that has been previously reported for Cd(II) and Co(II) ions in this study. The highest removal percentage was achieved with the BMM, then the AMM and RMN material. Huang and Lin (2015) and Vilar *et al.* (2008) have also reported the same trend of increased removal of Cu(II) ions as the solution pH was increased, using agricultural waste biosorbents. Compared with the Cd(II) and Co(II) removal, the *Macadamia* based biosorbents showed higher affinity for Cu(II) ions. The percent removal for Cu(II) was close to 70% whereas it was less than 25% for Co(II) and Cd(II). This was confirmed by comparing the removal of Cu(II) [Mw = 63.5 g/mol], Co(II) [Mw = 58.9 g/mol] and Cd(II) [Mw = 112.4 g/mol] ions on the basis of mole ratios. The amount adsorbed (adsorption capacity) at the highest removal pH for Cu(II)

was found to be 0.200, 0.156 and 0.129 mmol/g for the BMM, AMM and RMN adsorbents, respectively. For Co(II) it was 0.084, 0.060 and 0.045 mmol/g for the BMM, AMM and RMN adsorbents, separately. These values are comparable with those of Cd(II) which are 0.046, 0.05 and 0.048 mmol/g for the BMM, AMM and RMN adsorbents, respectively. These results demonstrated that the preference order for adsorption was Cu(II), Co(II) and lastly, Cd(II). Cu(II) and Co(II) have similar molar masses while Cd(II) is almost twice the size, therefore it can be concluded that the size of the metal ion played a role in their removal by the *Macadamia* based adsorbents.

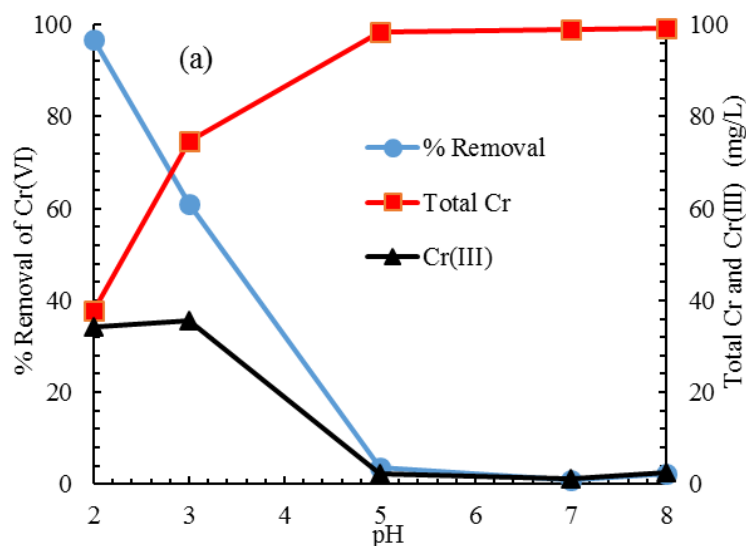
5.2.4 The effect of solution pH for Cr(VI) adsorption

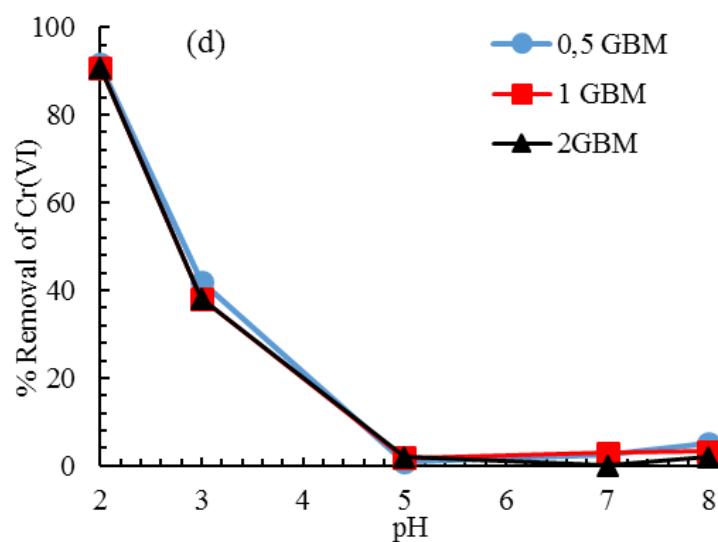
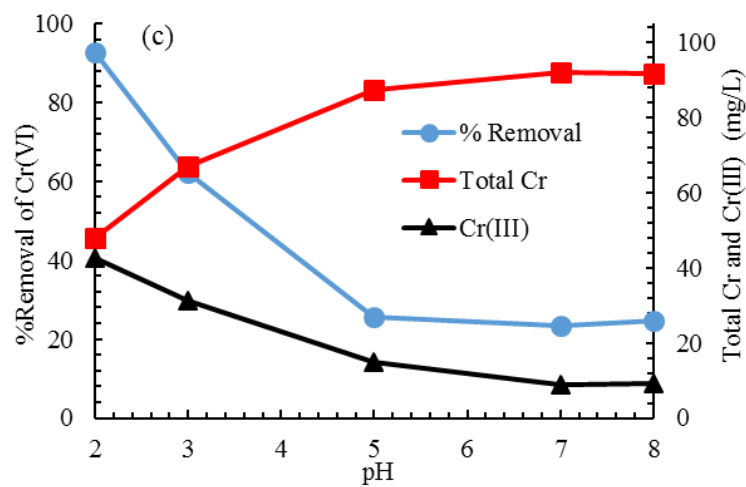
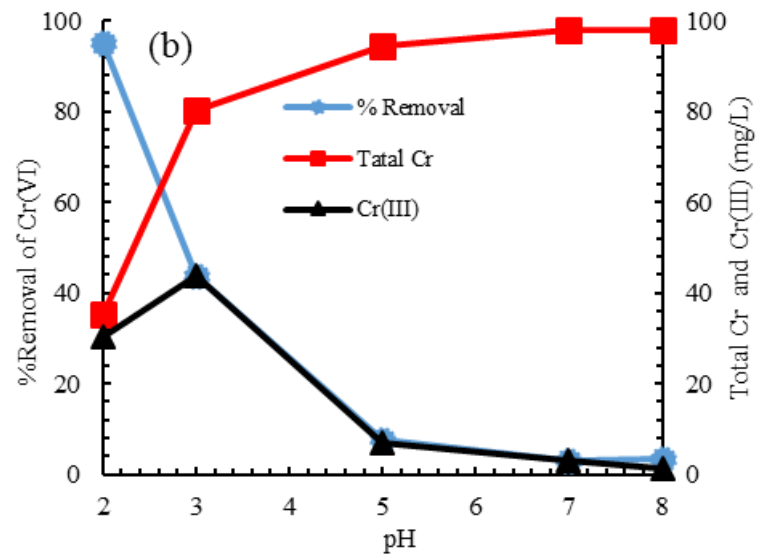
Figure 5.13 (a–e) depicts the percentage removal of Cr(VI) by the different *Macadamia* based biosorbents as a function of pH and Figure 5.13 (a–c) also shows the equilibrium concentration of Cr(III) and total Cr after adsorption. A pH curve different to that which was observed for the cations in section 5.10 to 5.12 was observed for the percent removal of Cr(VI). In this instance, the percent removal decreased as the pH of the solution was increased from pH 2 to pH 5 then no notable change was observed afterwards. The highest percent removal was realized at pH 2 for all materials. The high removal of Cr(VI) at acidic conditions was also described by other researchers (Park *et al.*, 2007; Ng *et al.*, 2016).

In aqueous solution, Cr(VI) exists as an anionic species in the form of HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ or $\text{Cr}_2\text{O}_4^{2-}$ depending on the pH of the solution and concentration (Garg *et al.*, 2007). According to Gebrehawaria *et al.* (2015), the hydrolysis reaction of $\text{Cr}_2\text{O}_7^{2-}$ in acidic conditions shifts the equilibrium of chromate species to HCrO_4^- .

Therefore, it is normally the dominant HCrO_4^- species that gets electrostatically attracted to positively charged sites of the adsorbent in acidic conditions.

The decrease of Cr(VI) removal at pH 3 could be attributed to the shift of equilibrium between chromate species. For an example, formation of more bulky species like $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ or $\text{Cr}_2\text{O}_4^{2-}$ than HCrO_4^- . The presence of these bulky substrates could lead to steric hindrance and less adsorption. From pH 5 onwards, the decrease in %Cr(VI) removal was attributed to competitive adsorption of Cr(VI) anions and OH^- ions from NaOH used for pH adjustment. Another contributing factor could be that, as the pH was increased the surface moieties got deprotonated and that resulted in electrostatic repulsion between the Cr(VI) anions and the adsorbent surface.





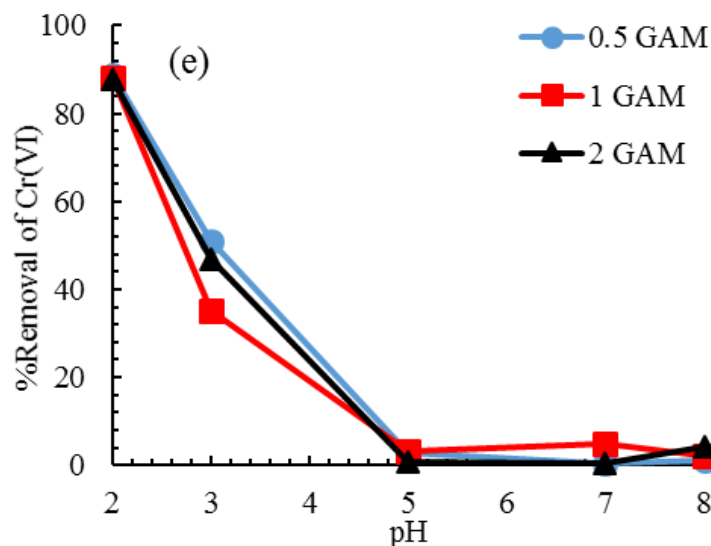


Figure 5.13: Effect of pH for RMN (a), AMM (b), BMM (c), 0.5 GBM, 1 GBM, and 2 GBM (d), 0.5 GAM, 1 GAM, and 2 GAM (e). Adsorption conditions (contact time 120 min, initial concentration 100 mg/L, and adsorbent mass 0.1 g).

Saha and Orvig (2010) proposed four mechanisms explaining how Cr(VI) ions were sequestered by biosorbents. The first involves the adsorption of anionic Cr(VI) to the protonated adsorbent sites, through electrostatic attraction. The second possibility involves the adsorption of Cr(VI) followed by its subsequent reduction to less toxic Cr(III). In the third possibility, part of Cr(VI) gets adsorbed while another portion of Cr(VI) is reduced to Cr(III) which is in turn adsorbed by the biosorbent. The last mechanism involves the adsorption of Cr(VI) while another fraction of Cr(VI) is reduced to Cr(III) at the surface of the adsorbent and then released back into solution. The electron-donor groups adjacent to the binding site are responsible for initiating the reduction of Cr(VI) to Cr(III) according to the following redox reactions.



In Figure 5.13 (a–c), the total chromium concentration at pH 2 was not zero or even close to zero because it symbolized that not all the Cr(VI) ions were adsorbed but some part of it was transformed into Cr(III). Therefore, the *Macadamia* based biosorbents followed the adsorption–reduction mechanism. From Figure 5.13 (a–c), the amount of Cr(III) in solution after adsorption was higher for the BMM (40 mg/L), followed by RMN (37 mg/L) and lastly AMM (30 mg/L). This revealed that the acid treatment of RMN material removed more electron–donor groups than the base treatment method. However, all materials were capable of removing more than 95% of Cr(VI) even though part of it was reduced to less toxic Cr(III). Also, noteworthy to mention is the decrease in percent removal of Cr(VI) at pH 2 when the GAM and GBM grafted materials were used. This was attributed to the extraction of acid soluble functionalities during acrylic acid grafting or blockage of adsorption sites as a result of grafting.

The FTIR spectra of the GAM and GBM grafted materials showed a decrease in the intensity of the carbonyl group band at approximately 1700 cm^{-1} . Therefore, this diminishing character can be attributed to the extraction of acid groups during grafting leading to decrease in the electron donating groups thus lowering the adsorption capabilities of the biosorbents. Grafting of BMM and AMM with different concentrations of acrylic acid displayed no noticeable difference in the adsorption of Cr(VI). Because of these insignificant differences in Cr(VI) removal by the different grafted materials (0.5 GAM, 1 GAM, 2 GAM) for the AMM material and (0.5 GBM, 1 GBM, 2 GBM) for the BMM material, only the 0.5 GAM and 0.5 GBM adsorbents were evaluated in further adsorption studies.

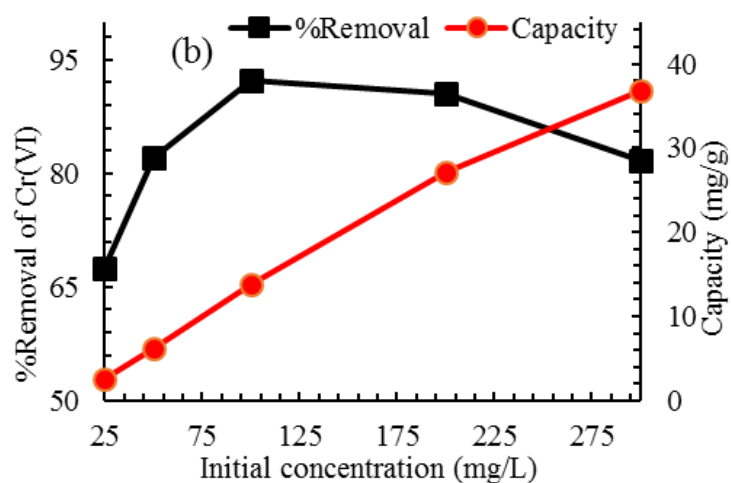
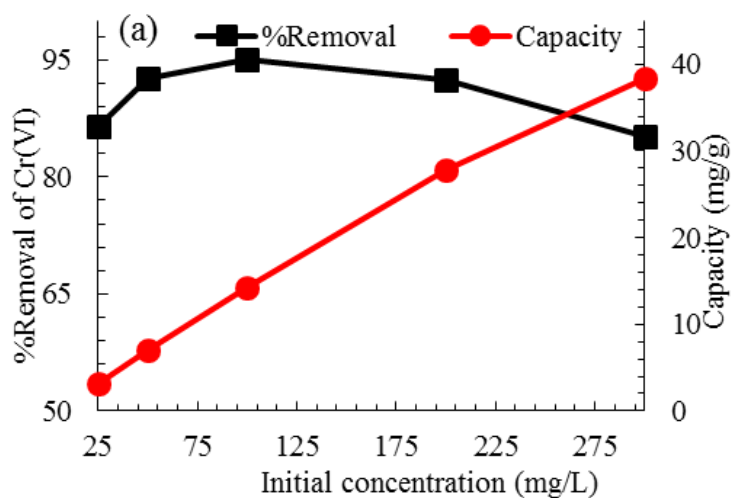
Furthermore, the pH of the solution was measured before and after the adsorption of Cr(VI) and an increase in pH was observed. The increase in pH of the solution after adsorption suggested that protons may have been depleted at $\text{pH} > 7$ (Park *et al.*, 2007). This may clarify why all the materials after the different chemical treatments had a lower Cr(VI) removal percentage than the RMN material. The pH_{PZC} of the different biosorbents can be used to explain the proton depletion and subsequent lower removal for the chemically treated materials. Firstly, the AMM and BMM materials had a higher pH_{PZC} than the RMN material. The 0.5 GBM, 1 GBM, and 2 GBM grafted from the BMM material had a higher pH_{PZC} than the BMM material. The trend was the same with the AMM grafted materials 0.5 GAM, 1 GAM, and 2 GAM, meaning that as the pH_{PZC} of the respective material increased the materials were more deprotonated thus resulting in lower Cr(VI) removal percentage.

The RMN, AMM and BMM materials demonstrated a greater affinity for Cr(VI) than they did for Cd(II), Co(II), and Cu(II). The percent removal for Cu(II) was close to 70%, that of Cd(II) and Co(II) were less than 30%. Thus, for subsequent adsorption experiments, only Cr(VI) was considered since the RMN, AMM, and BMM adsorbents showed greater removal efficiency for Cr(VI). In addition, the adsorption properties of the acrylic acid grafted biosorbents were also evaluated using Cr(VI) adsorbate, which was found to have more than 95% removal of Cr(VI). Thus, for all further adsorption experiments of Cr(VI) only the RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM materials were evaluated.

5.2.5 Effect of initial concentration

The effect of initial adsorbate concentration on the removal of Cr(VI) by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM biosorbents is portrayed in Figure 5.14(a–c). The initial concentration of Cr(VI) was varied from 25 to 300 mg/L while all other adsorption parameters were kept constant. It can be observed that at lower concentrations (25 – 100 mg/L) the percent removal of Cr(VI) increased, but from 100 mg/L to 300 mg/L the percent removal decreased for RMN, AMM, and BMM adsorbents [Figure 5.14(a–c)]. The decrease in percent removal at higher initial concentration is attributed to the saturation of adsorption sites (Owalude and Tella 2016). On the other hand, the 0.5 GAM and 0.5 GBM adsorbents displayed a different adsorption trend than the RMN, AMM, and BMM adsorbent. The adsorption of Cr(VI) ions using 0.5 GAM and 0.5 GAM adsorbents decreased as the initial concentration of Cr(VI) ions increased from 25 to 300 mg/L. This is because at low concentration there are more adsorption sites available for the Cr(VI) ions to occupy them. Nonetheless, at high concentrations of Cr(VI) the adsorption sites are not sufficiently available. Thus, the percent removal decreases due to the saturation of adsorption sites (Mekonnen *et al.*, 2015). Of note is that, for all the adsorbents the adsorption capacity increased as the initial Cr(VI) concentration was increased in this order 0.5 GBM (5.24–41.27 mg/g) > 0.5 GAM (4.68–40.81 mg/g) > RMN (3.24–38.31 mg/g) > AMM (2.53–36.76 mg/g) > BMM (2.75–35.25 mg/g). The 0.5 GAM and 0.5 GBM adsorbents had a significantly higher adsorption capacities than the RMN, AMM and BMM adsorbents. This could be due to the increased electron donors on the surface caused by the addition of acrylic acid moieties. The RMN, AMM and BMM

adsorbents achieved highest percent removal at 100 mg/L while 0.5 GAM and 0.5 GBM showed highest percent removal at 25 mg/L. Therefore, those concentrations were used for subsequent experiments.



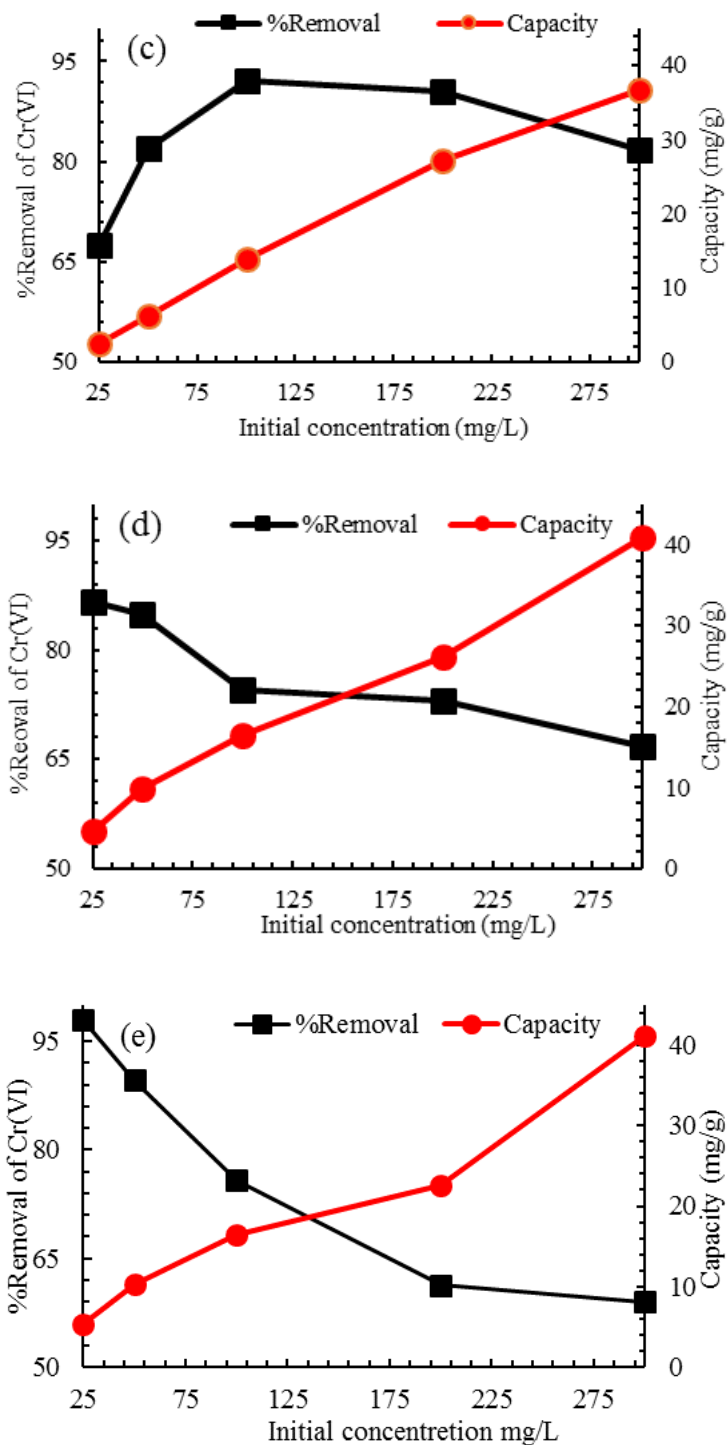


Figure 5.14:Effect of initial Cr(VI) concentration for RMN (a), AMM (b), BMM (c), 0.5 GAM (d), and 0.5 GBM (e). Adsorption conditions (pH 2, contact time 120 min, adsorbent mass 0.1 g, initial Cr(VI) concentration 100 mg/L).

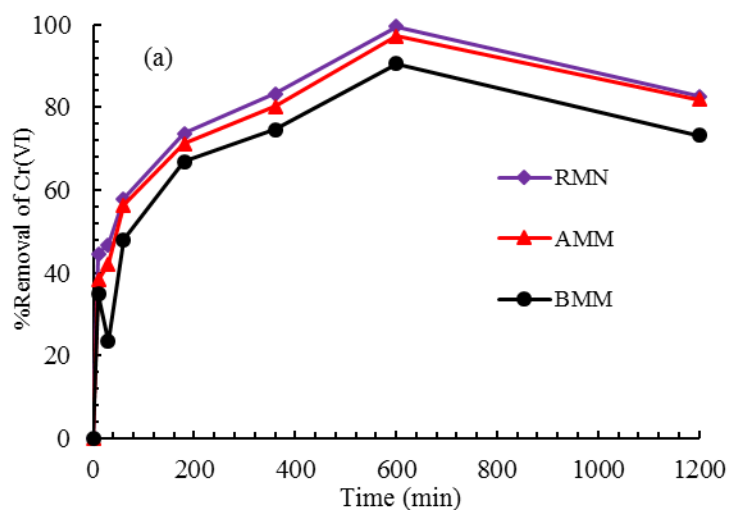
5.2.6 Effect of contact time

The adsorption of Cr(VI) ions as a function of contact time by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM adsorbents is represented in Figure 5.15(a–c). The contact time was varied from 10 to 1200 min while all other parameters were kept constant. The percent removal of Cr(VI) increased as the contact time was increased this was observed for all the adsorbents. From 10 to 180 min the removal of Cr(VI) was rapid reaching 73.74%, 71.19%, and 66.87% removal for RMN, AMM, and BMM, respectively. From 180 to 600 min the adsorption increased by about 20% for all the three materials, indicating that after 180 min the adsorption rate became slow. Researchers such as Mekonnen *et al.*, (2015); Kaya *et al.*, (2014) who used wheat bran and papaya peels, respectively, for the removal of Cr(VI) from an aqueous solution also obtained a similar trend. The adsorption rate was said to be faster before the reaction reached equilibrium and slower as the reaction attained equilibrium. It can be noted that after 600 min the adsorption decreased, a phenomenon credited to the saturation of adsorption sites and the desorption of Cr(VI).

Similarly, the removal of Cr(VI) by the grafted materials was more rapid in the first 180 min achieving 95.48% and 98.06% removal efficiencies for the 0.5 GAM and 0.5 GBM adsorbents, respectively as depicted in Figure 5.15. The equilibrium was accomplished after 180 min for both materials with the removal percentage reaching 100%. The grafted materials did not show a decrease in the adsorption of Cr(VI), as it was observed with the RMN, AMM, and BMM materials. The availability of adsorption sites contributed to the faster adsorption rate for the first 180 min. The slow adsorption rate after 180 min was due to the limited number of adsorption sites coupled

with the electrostatic hindrance due to the presence of Cr(VI) on the adsorbent surface leading to the slow diffusion Cr(VI) ions to the inner adsorption sites (Goswami and Ghosh, 2005).

The grafted materials displayed faster Cr(VI) removal kinetics than the RMN, AMM, and BMM materials because of the surface functional groups attached. However, the 0.5 GAM appeared to reduce Cr(VI) to Cr(III) more than 0.5 GBM as demonstrated by the lesser amount of Cr(III) remaining in solution as observed in Figure 5.15(b) and Figure 5.15(c), respectively. This corresponds to previous data that the acid treated biosorbents have more reducing power than the base treated biosorbents. The optimum contact time for the RMN, AMM, and BMM was 600 min while that of the 0.5 GAM and 0.5 GBM was 180 min.



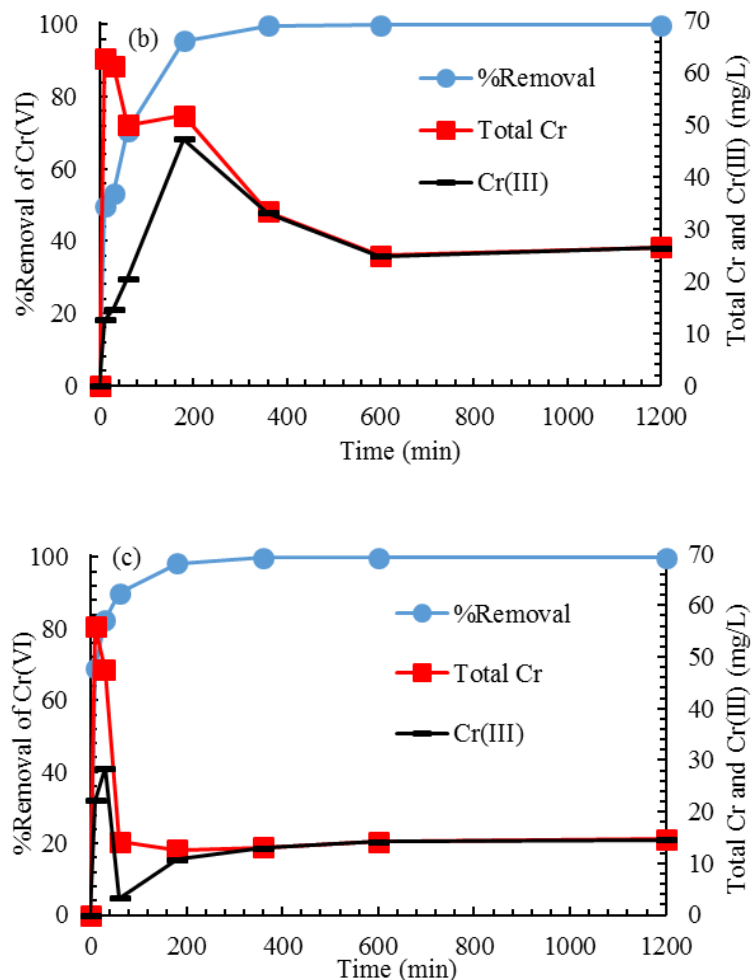


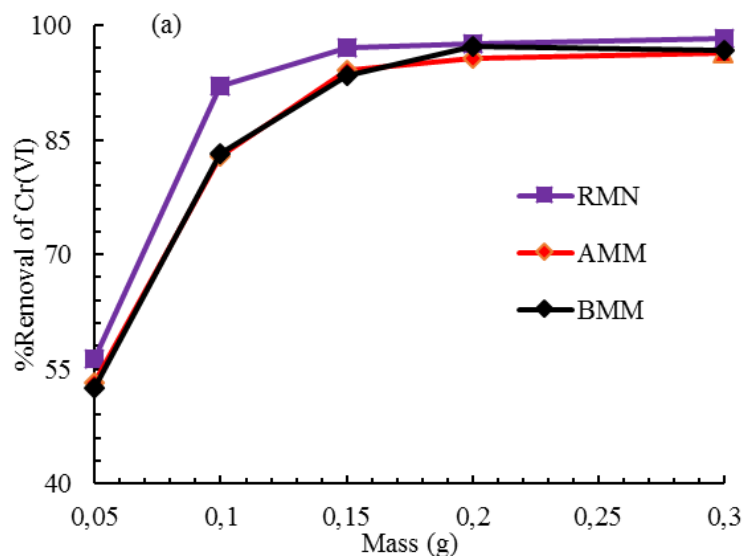
Figure 5.15: Effect of contact time for the adsorption of Cr(VI) by RMN, AMM, and BMM (a), 0.5 GAM (b), and 0.5 GBM (c) material. Adsorption conditions (pH 2, initial Cr(VI) concentration 100 mg/L and 25 mg/L, adsorbent mass 0.1g).

5.2.7 The effect of adsorbent mass

The effect of adsorbent mass on the adsorption of Cr(VI) ions onto RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM materials was studied by varying the biosorbent mass from 0.05 to 0.3 g while keeping all other parameters constant. Figure 5.16 (a–c) displays the percentage removal of Cr(VI) as a function of adsorbent mass. The percent removal of Cr(VI) increased as the adsorbent mass was increased for all the

biosorbents and reached a plateau. The increase in percent removal as the mass increased, was attributed to the additional adsorption sites imparted by increasing the adsorbent mass (Qi *et al.*, 2016). The maximum adsorbent mass was 0.2 g for the RMN, AMM, and BMM materials 0.15 g for the 0.5 GAM and 0.5 GBM materials.

The 0.5 GAM and 0.5 GBM biosorbents were selected to show the reduction of Cr(VI) to Cr(III). As the percent removal of Cr(VI) increased by increasing the adsorbent mass, the Cr(III) remaining in solution was also increased and reached equilibrium at 0.15 g for both materials as shown in Figure 5.16 (b) and Figure 5.16 (c). This indicated that not all the Cr(VI) was removed from solution but part of it was reduced to Cr(III). Again as demonstrated previously the acid treated materials showed more reduction capabilities than the base treated materials as indicated by the amounts of Cr(III) left in solution as it can be seen in Figure 5.16 (b) and (c).



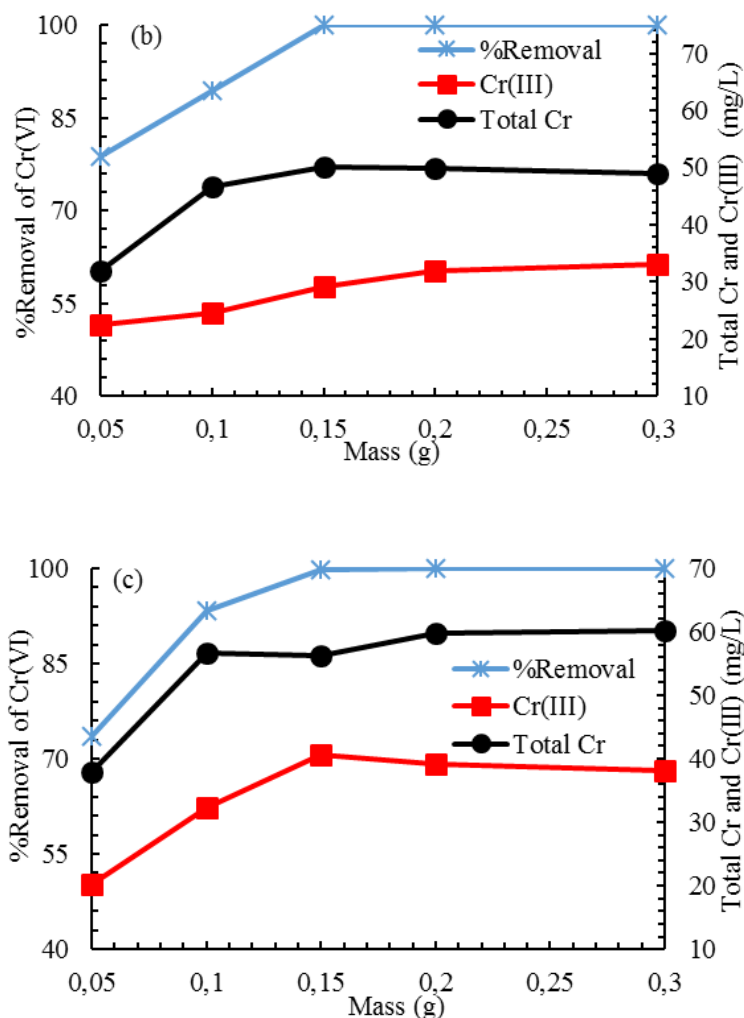


Figure 5.16: Effect of adsorbent mass for the adsorption of Cr(VI) by RMN, AMM, and BMM (a), 0.5 GBM (b), and 0.5 GAM (c) materials. Adsorption conditions (pH 2, time 600 and 180 min, initial concentration of Cr(VI) 100 and 25 mg/L, adsorbent mass 0.2 and 0.15 g and sample volume 20 mL).

5.2.8 The effect of temperature

The temperature effect on the adsorption of Cr(VI) using RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM biosorbents was explored by varying temperature between 20 and 40°C. The results are depicted in Figure 5.17(a–c). The percent removal of Cr(VI) ions

increased as the temperature increased. The increase in the adsorption of Cr(VI) ions was attributable to the decrease in the viscosity of the solution, which resulted in an increase in the molecular motion (Aksu, 2001). The increased percent removal as a function of temperature implied that the boundary thickness of the surface of the adsorbent did not decrease at high temperatures. The thinning of the boundary layer would have led to the weakening of the interaction between the adsorbent and the Cr(VI) ions (Horsfall Jnr and Spiff, 2005). In this case, 40°C gave the best removal for Cr(VI) for all adsorbents.

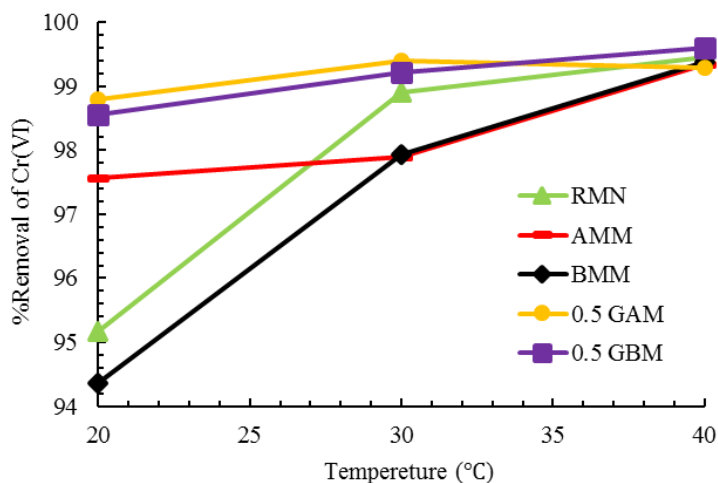


Figure 5.17: Effect of temperature on the adsorption of Cr(VI) by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM. Adsorption conditions (pH 2, contact time 600 and 180 min, initial Cr(VI) concentration 100 and 25 mg/L, adsorbent mass 0.2 and 0.15 g).

5.2.9 The effect of co-existing anions

The adsorption of Cr(VI) by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM biosorbents in the presence of co-existing anions (chlorides, hydroxides, sulfates, phosphate and

nitrate) is shown in Figure 5.18. It can be observed that the percent removal of Cr(VI) was not negatively affected by the presence of competing anions. For the RMN material, the percent removal of Cr(VI) was the same in the presence of competing ions and in blank solutions. It was expected or anticipated that the addition of the anions would decrease the percent removal of Cr(VI). Since both the Cr(VI) and the added anions carry a negative charge, they would compete for the positive adsorption sites on the adsorbents and result in a decrease in the adsorption of Cr(VI) (Bhaumik *et al.*, 2014). But the trend was opposite, having a high removal of Cr(VI) in the presence of anions than in the absence of competing anions.

The phenomena can be attributed to the possibility of Cr(VI) reduction to more positively charged Cr(III) species. Bearing in mind that as the adsorption of Cr(VI) takes place both the Cr(VI) anions and the competing anions get attracted to the surface of the adsorbent. Thus, creating more negatively charged adsorbent surface, leading to electrostatic attraction of the Cr(III) ions. This phenomenon was not observed for the RMN material since the percent removal of Cr(VI) was the same in the presence of competing anions and in the blank. The different chemical treatment methods may have contributed to this phenomenon not taking place for the RMN material.

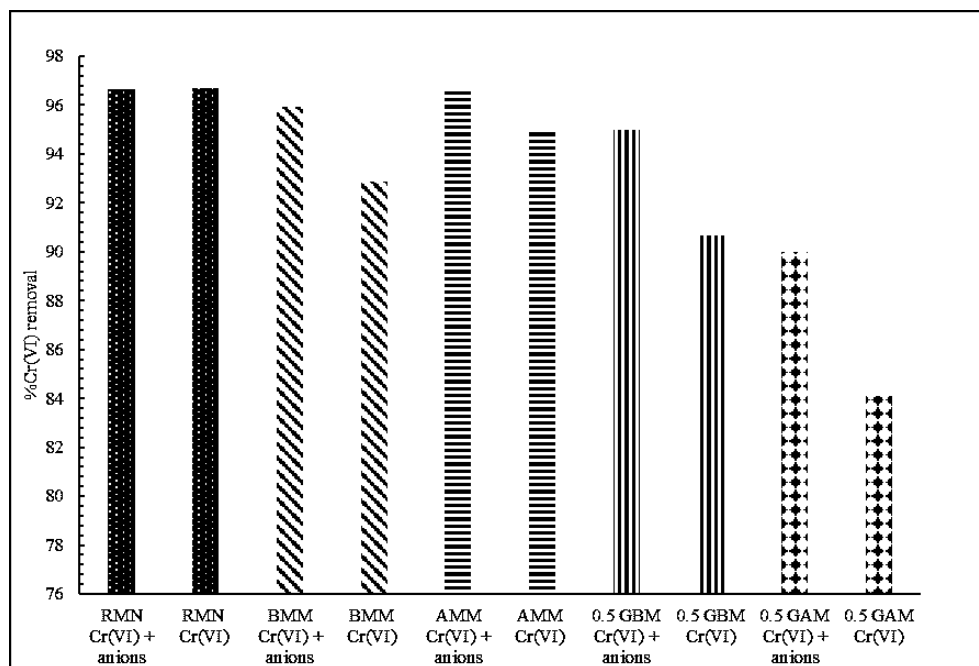


Figure 5.18: Effect of competing anions upon the adsorption of Cr(VI) by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM materials. Adsorption conditions (pH 2, contact time 600 and 180 min, adsorbent mass 0.2 and 0.15 g, and initial Cr(VI) ions concentration 100 and 25 mg/L).

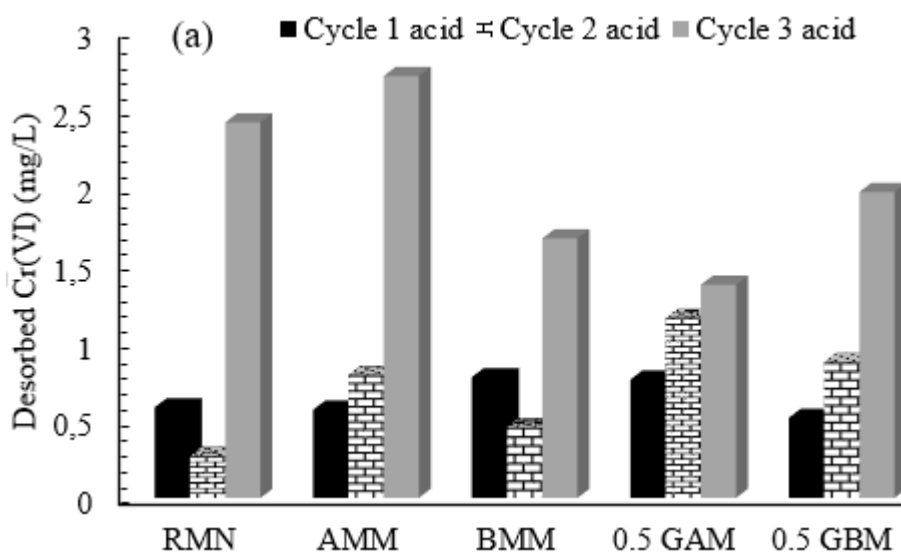
5.2.10 Desorption/ adsorbent regeneration

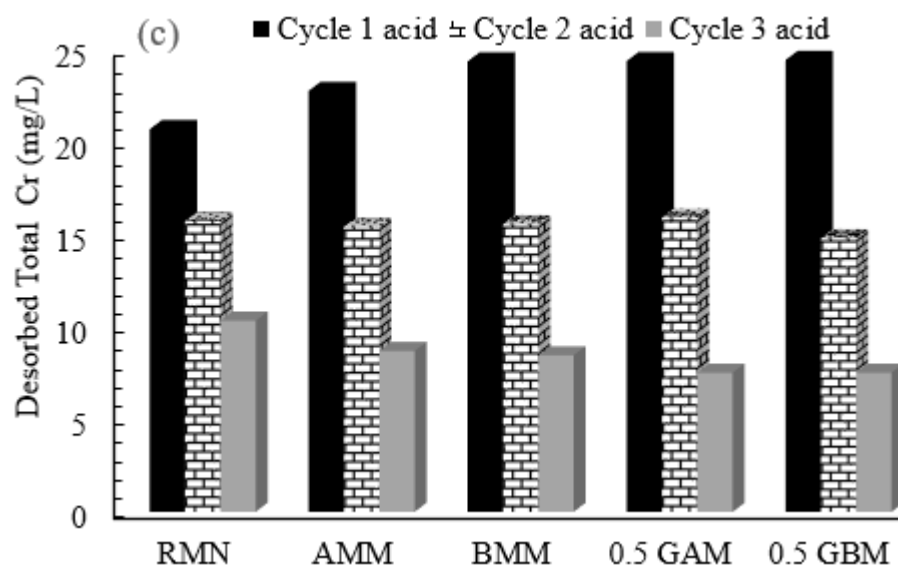
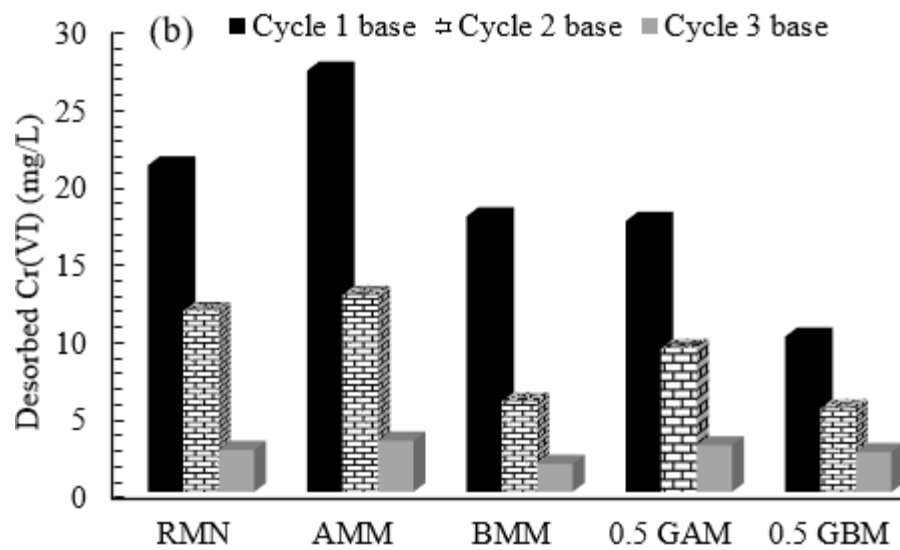
Adsorbent regeneration by desorbing the metal ions loaded on the surface of the adsorbent is a critical part of the adsorption process. The adsorbents (RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM) loaded with Cr(VI) anions underwent three separate cycles of Cr(VI) desorption by either 0.1 M HCl or 0.1 M NaOH as desorption reagents. After each desorption cycle the final concentration of Cr(VI), Cr(III), and total Cr were determined. The results are shown in Figure 5.19. The initial concentration of Cr(VI) used in all reactions was 100 mg/L.

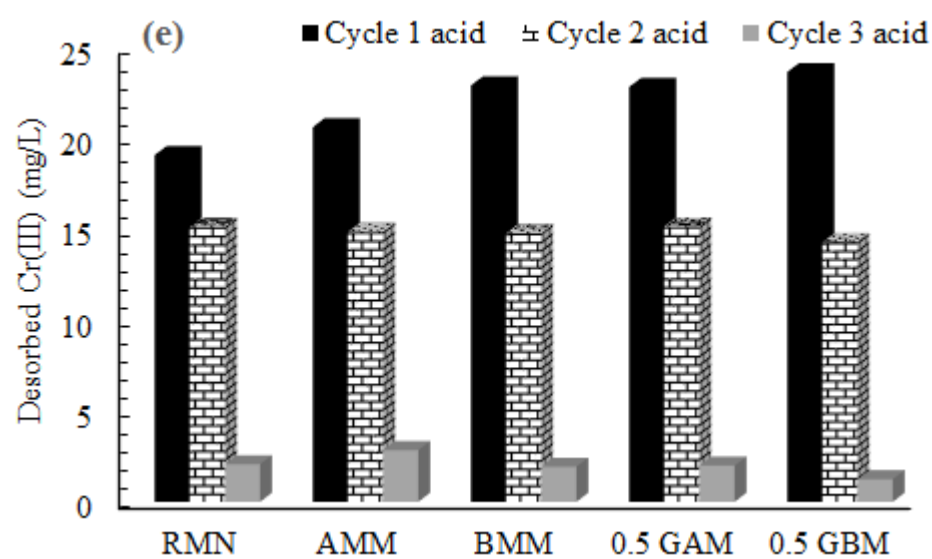
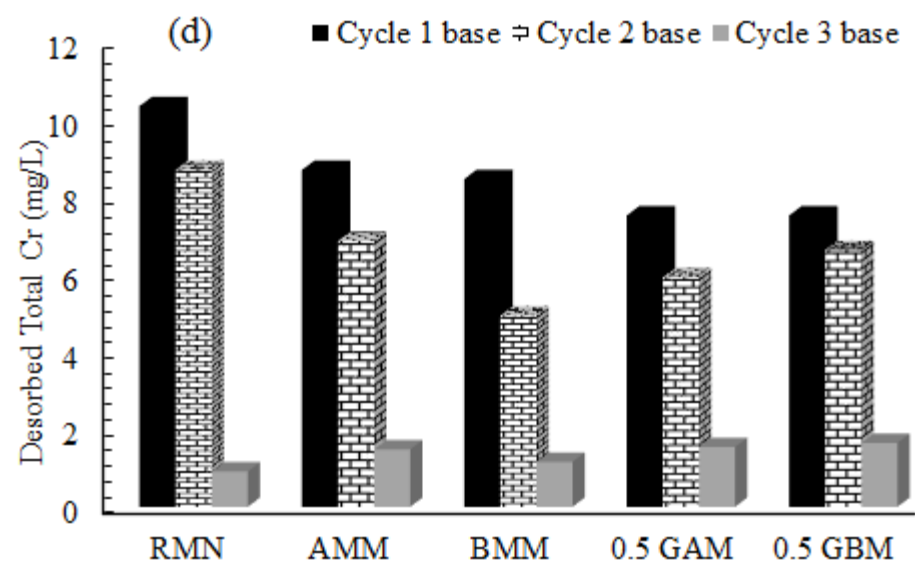
The desorption of Cr(VI) using 0.1 M HCl did not show a uniform trend for all the materials. For the AMM, 0.5 GAM, and 0.5 GBM the Cr(VI) desorption increased as the number of desorption cycles was increased (Figure 5.19 a). In the case of the RMN and BMM materials, the Cr(VI) desorption decreased during the second cycle and it increased in the third cycle. The desorbed concentration was found to be less than 3 mg/L for all the materials, indicating that 0.1 M HCl was a poor desorbing agent for Cr(VI). Nonetheless, Dehghani *et al.* (2016) used HCl for the desorption of Cr(VI) on treated waste newspaper and a 78% desorption rate was reported.

In Figure 5.19 (b), it can be deduced that the amount of Cr(VI) desorbed using 0.1 M NaOH decreased as the number of cycles was increased in all materials. The desorption was most efficient for AMM>RMN>BMM>0.5 GAM>0.5 GBM with respective highest desorption amount of Cr(VI) equaling 28, 21, 19, 18, and 10 mg/L, respectively. The NaOH solution desorbed more Cr(VI) ions than the HCl solution. To explain the possible desorption mechanism that led to the base desorbing more Cr(VI) than the acid, it can be considered that after adsorption of Cr(VI) both Cr(VI) and Cr(III) can be present on the adsorbent. The presence of Cr(VI) and Cr(III) on the surface of *Chlorella vulgaris* biomass after the adsorption of Cr(VI) were reported by Xie *et al.* (2014) using X-Ray photoelectron spectroscopy (XPS) analysis. In the present study, the desorption of Cr(VI) was followed up by UV-Vis and AAS spectroscopic methods. When the adsorbent loaded with Cr(VI) and Cr(III) was treated with HCl the surface moieties were protonated. This led to the electrostatic attraction of Cr(VI) ions whilst the Cr(III) ions were displaced into the solution (Wankasi *et al.*, 2005).

The same remains true when the loaded adsorbent was treated with NaOH, the Cr(III) ion remained bound to the surface and while Cr(VI) ions were displaced into the solution as a result of adsorbent deprotonation. The higher desorption of Cr(VI) by NaOH may be attributed to the presence of more Cr(VI) ions than the Cr(III) ions on the surface of the adsorbent. This notion that the HCl displaced Cr(III) and the NaOH displaced Cr(VI) was supported by the determination of Cr(III) ions after each desorption cycle depicted in Figure 5.19 (c and d). It can be observed that the presence of Cr(III) was more prevalent when the materials were desorbed with HCl than with NaOH.







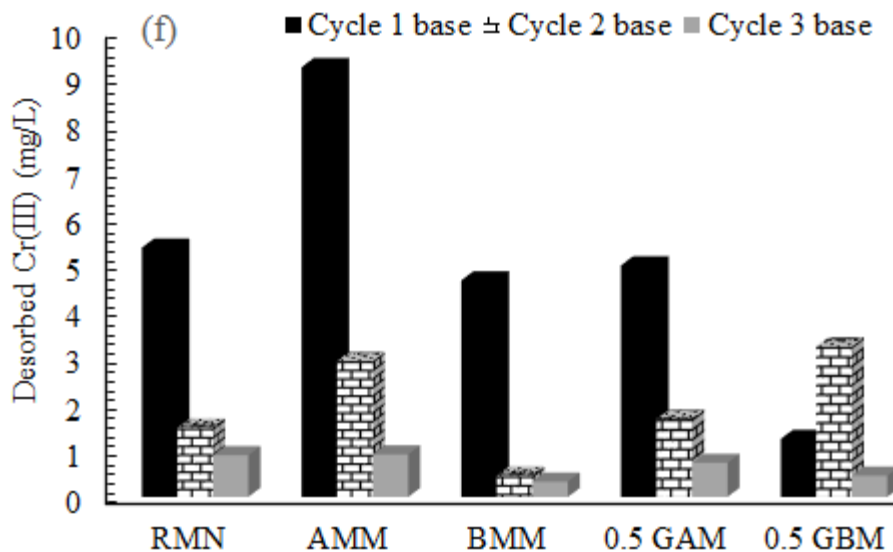


Figure 5.19: Desorption of Cr(VI) from RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM biosorbents by monitoring the final concentration of Cr(VI) using HCl (a) and NaOH (b), total Cr HCl (c) and NaOH (d) and Cr(III) HCl (e) and NaOH (f).

5.3 Experimental data modeling

The experimental data of the different adsorption parameters such as the effect of initial concentration, contact time, and temperature were fitted into different adsorption models. The data modeling provides an understanding regarding the chemical and physical interactions between the adsorbent and the adsorbate. Information such as adsorption mechanism and the nature of the adsorption process can be extrapolated from the mathematical equations of the adsorption isotherms, kinetics, and thermodynamics of the reaction.

5.3.1 Adsorption isotherms

The equilibrium performance between various *Macadamia* based adsorbents and the Cr(VI) species has been articulated by employing the two most commonly used adsorption isotherms Langmuir and Freundlich (Tutu *et al.*, 2013; Mekonnen *et al.*, 2015). The Langmuir isotherm is based on the assumption that the adsorption follows a monolayer coverage of the adsorbent by the adsorbate (Langmuir, 1918) on homogenous adsorption sites. The Langmuir isotherm can be expressed in a nonlinear form as shown by equation 5.1

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad 5.1$$

where q_e is the amount of metal uptake (mg/g) at equilibrium, q_m is the maximum monolayer coverage capacity (mg/g). The equilibrium concentration is represented by C_e (mg/L), K_L is the Langmuir isotherm constant (L/mg). The values of q_m and K_L were obtained from the slope and intercept of a linear plot of $\frac{1}{q_e}$ against $\frac{1}{C_e}$.

The equilibrium parameter R_L or separation factor is one of the important parameters used to explain adsorbate-adsorbent interaction likelihood (Weber and Chakravorti, 1974). It is a dimensionless constant, where $0 < R_L < 1$ represents a favorable adsorption and the reaction is regarded as unfavorable. If R_L is greater than 1 then the reaction is linear and if R_L is equal to zero the reaction is irreversible. The value of R_L can be obtained by using equation 5.2.

$$R_L = \frac{1}{(1 + K_L C_o)} \quad 5.2$$

where C_0 is the initial concentration (mg/L) and K_L is as described previously.

The Freundlich isotherm describes the adsorption process as a multilayer adsorption on a heterogeneous surface. The Freundlich isotherm can be expressed in a nonlinear form as shown by equation 5.3

$$q_e = K_f C_e^{\frac{1}{n_f}} \quad 5.3$$

where K_f is the Freundlich constant $[(\text{mg/g})/(\text{mg/L})^{1/n}]$ and n_f is the intensity.

Nonlinear forms of the models equations were used to plot the data using KyPlot 2.0 software (quasi-Newton algorithm). Table 5.3 portrays the Langmuir and Freundlich isotherms equilibrium parameters for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM adsorbents. The maximum adsorption capacities (q_m) were 54.99, 81.38, 59.67, 39.21, and 23.93 for RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM, respectively. The trend for the q_m values followed that of the experimental adsorption capacity (q_e), but the values are lower than that of the q_m values. The Langmuir equilibrium constant (K_L) increased from 0.016 to 0.079 L/mg in this order AMM<BMM<0.5 GBM<RMN<0.5 GAM, implying that the Cr(VI) ions had a more preferential binding for the RMN and 0.5 GAM adsorbents (Pakade et al., 2016). The Freundlich K_f values which also indicate the adsorption capacity showed that the adsorption capacity was very low for all the materials.

The obtained values for n_f were greater than unity resulting in $\frac{1}{n_f}$ values between 0 and 1 representing a favorable adsorption process in this order 0.5 GBM>0.5 GAM>RMN>BMM>AMM. The RMN, AMM, BMM, and 0.5 GAM materials

showed a higher correlation of determination (r^2) value for the Langmuir model whilst the 0.5 GBM adsorbent showed a higher r^2 value for the Freundlich model. The difference in model preference could be an attribute of the different chemical treatment methods that the adsorbents were exposed to. This indicates that the acid, base, and grafting treatments resulted in the materials having different surface characteristics. Hence, the adsorption mechanism was influenced by the surface properties of the adsorbents. Therefore, equilibrium isotherm parameters for the adsorption of Cr(VI) ions indicate that the experimental data fitted well the Langmuir model.

Table 5.3 Equilibrium isotherm parameters for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM.

		Adsorption isotherms				
Model	Parameters	RMN	AMM	BMM	0,5 GAM	0,5 GBM
Langmuir	q_e (exp) (mg/g)	38,31	36,75	35,25	40,81	41,27
	q_m (mg/g)	54,99	81,38	59,67	39,21	23,93
	K_L (L/mg)	0,056	0,016	0,024	0,079	0,052
	r^2	0,947	0,869	0,910	0,975	0,933
	Total sum of squares	88.89	134.88	97.50	40.45	6.34
Freundlich	q_e (exp) (mg/g)	38,31	36,75	35,25	40,81	41,27
	K_f (mg/g)	4,860	1,975	2,604	6,191	3,590
	n_f	1,796	1,345	1,569	2,619	2,684
	$1/n_f$	0,557	0,743	0,637	0,382	0,373
	r^2	0,897	0,838	0,869	0,945	0,974
	Total sum of squares	45.96	108.71	66.86	17.95	16.58

On the bases of the total sum of squares, the Langmuir model fitted more the 0.5 GBM owing to a lower error which was in contrast with the higher r^2 value for the same material. Conferring to the lower error value the Freundlich model fitted the 0.5 GBM and 0.5 GAM materials but the lower maximum adsorption capacity could not hold

the best fit argument since it was considerable lower than the one for Langmuir and the experimental one. Thus both all the materials RMN, AMM, BMM < 0.5 GBM, and 0.5 GBM were best fitted to the Langmuir model due to the r^2 value which was closer to 1, however, the maximum adsorption capacities are not closer to the experimental capacity.

The Langmuir separation factor (R_L values) for the RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM biosorbents are displayed in Table 5.4. It can be seen that all the R_L values are lesser than 1 and greater than zero an indication that the adsorption of Cr(VI) was favorable for all materials. The R_L values were closer to zero implying the likelihood of an irreversible reaction. This was attributed to the stronger bonds that may exist between the adsorbent surface and the Cr(VI) ions or that Cr(VI) was transformed into a different state (Cr(III)). Also, the R_L values decreased as the initial concentration was increased, a phenomenon that was related to stronger bonds between adsorbent and adsorbate as concentration increased. Goswami *et al.* (2014) also reported that as the initial concentration of Cr(VI) was increased, the R_L value decreased indicating a stronger bond interaction between Cr(VI) and the adsorbent.

Table 5.4: Langmuir separation factor for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM.

Initial concentration (mg/L)	Adsorbents				
	RMN	AMM	BMM	0,5 GAM	0,5 GBM
	R _L values				
25	0,41667	0,71429	0,62500	0,33613	0,43478
50	0,26316	0,55556	0,45455	0,20202	0,27778
100	0,15152	0,38462	0,29412	0,11236	0,16129
200	0,08197	0,23810	0,17241	0,05952	0,08772
300	0,05618	0,17241	0,12195	0,04049	0,06024

5.3.2 Adsorption kinetics

The effect of contact time data was utilized for the investigation of the adsorption kinetics. Two kinetic models were selected, the pseudo first-order and pseudo second-order rate models. The pseudo first-order also known as the Lagergren model, mainly describes the reaction process as taking place by metal ions diffusion through the adsorbent boundary layer (Lagergren, 1898). The equation can be expressed as follows

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad 5.4$$

where $K_1(\text{min}^{-1})$ is the rate constant and q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time (t), respectively. The pseudo second-order model describes the adsorption capacity on the solid phase and predicts chemisorption being the rate controlling step (Ho and McKay, 1998). It is represented by equation 5.5

$$q_t = \frac{tk_2q_e^2}{(1 + k_2q_e)} \quad 5.5$$

where k_2 is the rate constant (g/mg/min), q_e and q_t (mg/g) are as described previously.

The values of q_e , k_2 and h can be obtained from the slope and intercept of the plot of $\frac{t}{q_t}$ against time (t). The initial sorption rate (h) can be calculated from equation 5.6

$$h = k_2 q_e^2 \quad 5.6$$

The data for the pseudo first-order and pseudo second-order kinetic model for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM materials are represented in Table 5.5. The rate constant k_1 for the pseudo first-order model increased as follows 0.5 GBM<RMN<BMM<AMM<0.5 GAM. The trend indicated that the AMM and 0.5 GAM materials removed Cr(VI) ions faster than the other materials. The rate of reaction could not form a particular trend with the adsorption capacity of the pseudo first-order rate model. However, the experimental adsorption capacities have a similar trend with the adsorption capacity of the pseudo first-order model. With the 0.5 GAM and 0.5 GBM materials having the highest adsorption capacities in both cases.

The initial adsorption rate (h) increased in the order 0.5 GAM<AMM<0.5 GBM<BMM=RMN, demonstrating that the raw and the base modified materials (RMN, BMM and 0.5 GBM) had a faster initial adsorption rate than the acid-modified materials. The 0.5 GAM and 0.5 GBM materials had a faster pseudo second-order rate constant (k_2) at 0.0027 and 0.0092 (g/mg/min), respectively compared to the materials that were not grafted with acrylic acid. This suggests that the acrylic acid contributed to the rapid removal of Cr(VI) ions. The noted observation was supported by the effect of contact time experiments where it could be observed that both the 0.5 GAM and 0.5 GBM materials reached equilibrium faster than the RMN, AMM, and BMM materials

as depicted in Figure 5.15. The adsorption capacities for both isotherms were significantly lower than that of the experimental capacities. However, the materials with the highest k_2 values (0.5 GAM and 0.5 GBM) also showed higher experimental adsorption capacities.

This was attributed to the grafting of acrylic acid which subsequently improved the adsorption capacity of the *Macadamia* nutshell related to Cr(VI) removal. The correlation of determination (r^2) values for the pseudo second-order model were higher than the pseudo first-order r^2 values for all the materials. Therefore, the adsorption process followed a chemisorption reaction, and this was consistent with the kinetic data interpretation reported by Ali *et al.* (2016).

Table 5.5 Equilibrium kinetics parameters for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM.

		Adsorption kinetics				
		RMN	AMM	BMM	0,5 GAM	0,5 GBM
Pseudo first-order	q_e (mg/g)	38,31	36,75	35,25	40,81	41,27
	q_m (mg/g)	18,02	19,27	19,41	19,43	20,91
	k_1 (min^{-1})	0,018	0,028	0,023	0,031	0,116
	R^2	0,795	0,622	0,782	0,758	0,755
Pseudo second-order	q_e (mg/g)	38,31	36,75	35,25	40,81	41,27
	q_m (mg/g)	19,51	20,99	21,22	20,33	21,77
	k_2 (g/mg/min)	0,0012	0,0020	0,0017	0,0027	0,0092
	R^2	0,825	0,813	0,891	0,884	0,971

Table 5.6 exhibits the comparison of the adsorption capacities of various biosorbent materials. A direct comparison is practically impossible due to the diverse adsorbent treatment methods and optimum experimental conditions used. The *Macadamia*

nutshells powder that has been investigated in this study had comparable adsorption capacities to other biosorbents used for the removal of Cr(VI). The RMN had a much higher adsorption capacity than other untreated biosorbents such as papaya peels and wheat bran. Whilst the chemical modified *Macadamia* nutshells showed a higher adsorption capacity than other chemically treated biosorbents such as wheat bran, potato peelings, acrylonitrile grafted banana peels and Fe(III)-impregnated sugarcane bagasse. On the other hand, pyromellitic dianhydride treated groundnut shell and H₂SO₄ modified sugarcane bagasse showed a greater adsorption capacity to that of the *Macadamia* nutshells biosorbent. This was attributed to the different chemical properties that came with the different chemical treatment methods. The chemical modification of agricultural waste biosorbents can increase the adsorption capacity of the biosorbents.

Table 5.6: Comparison of the adsorption capacities of *Macadamia* based biosorbents with other biosorbent materials

Adsorbents	Treatment	qm (mg/g)	References
Chlorella Valgaris	-	43.3	(Xie <i>et al.</i> , 2014)
Papaya peels	untreated	7.16	(Mekonnen <i>et al.</i> , 2015)
Mango sawdust	untreated	58.82	(Vinodhini and Das, 2009)
Wheat bran	untreated	4.53	(Kaya <i>et al.</i> , 2014)
Wheat bran	Tartaric acid	5.28	(Kaya <i>et al.</i> , 2014)
Swietenia mahagoni shells	untreated	37.03	(Rangabhashiyam and Selvaraju, 2015)
Swietenia mahagoni shells	H ₂ SO ₄	47.61	(Rangabhashiyam and Selvaraju, 2015)
Swietenia mahagoni shells	H ₃ PO ₄	58.82	(Rangabhashiyam and Selvaraju, 2015)
Newspaper waste	NaHCO ₃	59.88	(Dehghani <i>et al.</i> , 2016)
Groundnut shell	Pyromellitic dianhydride	131.00	(Owalude and Tella, 2016)
Sugar cane biomass	H ₂ SO ₄	131.68	(Bahadur and Paramatma, 2014)
Potato peelings	HCl	3.28	(Mutongo <i>et al.</i> , 2014)
Banana peels	Acrylonitrile grafted	6.17	(Ali <i>et al.</i> , 2016)
Sugarcane bagasse	Fe(III)-impregnated	13.72	(Zhu <i>et al.</i> , 2012)
RMN	untreated	38.31	This study
AMM	HCl	36.75	This study
BMM	NaOH	35.25	This study
0.5 GAM	Acrylic acid grafted	40.81	This study
0.5 GBM	Acrylic acid grafted	41.27	This study

5.3.3 Thermodynamics

The thermodynamic nature of the adsorption process was investigated by subjecting the experimental data for the effect of temperature to thermodynamic calculations. Thermodynamic parameters such as the free Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the data obtained by varying the temperature. The ΔG° can be calculated using equation 5.7.

$$\Delta G^\circ = RT \ln K_d \quad 5.7$$

where ΔG° is the Gibbs's free energy change (kJ/mol), R is the universal gas constant 8.314 J/mol/K, T is the temperature (K), and K_d is the partition coefficient which can be calculated by equation 5.8

$$K_d = \frac{q_e}{C_e} \quad 5.8$$

where q_e (mg/g) and C_e (mg/L) are the capacity and concentration at equilibrium respectively. Then, since K_d is a dimensionless constant equation 5.8 could be expressed by equation 5.9

$$K_d = \frac{q_e}{C_e} \times \frac{V}{m} \quad 5.9$$

where V is the volume of the solution (L) and m is the adsorbent mass (g)

The ΔH° and ΔS° can be obtained from equation 5.10 by plotting $\ln K_d$ against $1/T$ commonly called the Van't Hoff plot. Where ΔH° and ΔS° can be determined from the slope and intercept respectively.

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad 5.10$$

Table 5.7 shows the thermodynamic parameters for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM adsorbents. The adsorption reaction was feasible and spontaneous as indicated by the negative values of ΔG° (Módenes *et al.*, 2017), with the exception of the BMM and 0.5 GBM materials at 20°C. This showed that the adsorption process was nonspontaneous for the BMM and 0.5 GBM materials at 20°C, meaning that higher temperatures were required for the reaction to be spontaneous. This was demonstrated when the temperature was increased from 30 to 40°C the reaction became spontaneous shown by the negative ΔG° . The adsorption process was found to be more favorable as the temperature of the reaction was increased as indicated by the positive values of enthalpy ΔH° (Mthombeni *et al.*, 2015). The effect of temperature is in agreement with the notion that the adsorption process was most dominant as the temperature was increased as seen in Figure 5.17. The positive values of ΔH° also indicated that the adsorption process was endothermic (Ho, 2003).

The positive values of ΔS° points toward the increased affinity of the adsorbent and adsorbate and their subsequent structural changes (Gupta, 1998; Labidi *et al.*, 2016). This could be explained using Figure 5.6 and 5.7 of the XRD patterns for the adsorbents before and after adsorption of Cr(VI) ions, where the peak around $2\theta=10^\circ$ in Figure 5.6 was missing in Figure 5.7. This can indicate that structural changes of the adsorbents surface took place. The structural changes of the Cr(VI) ions could be

explained by the presence of Cr(III) ions in solution after the adsorption of Cr(VI) because of the reduction of Cr(VI) to Cr(III).

Table 5.7: Thermodynamic parameters for the adsorption of Cr(VI) ions by RMN, AMM, BMM, 0.5 GAM, and 0.5 GBM

Adsorbent	Thermodynamic parameters			
	T (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/(mol K))
RMN	293	-4,28	139,08	0,50
	303	-15,65		
	313	-13,92		
AMM	293	-3,53	91,98	0,32
	303	-4,76		
	313	-10,10		
BMM	293	0,18	149,19	0,51
	303	-4,90		
	313	-9,99		
0,5 GAM	293	-7,23	37,50	0,15
	303	-9,61		
	313	-10,27		
0,5 GBM	293	0,89	153,47	0,53
	303	-10,17		
	313	-9,39		

Similar thermodynamic parameters that indicate a feasible and spontaneous adsorption, endothermic adsorption reaction and a positive disorder were reported by (Zhu *et al.*, 2012) on the adsorption of Cr(VI) from aqueous solution using sugarcane bagasse.

Chapter six

6.1 Conclusions

Raw and chemically modified *Macadamia* nutshell powder were investigated for the adsorption of selected trace metal ions from aqueous solution in batch experiments. The *Macadamia* based adsorbents were characterized by FTIR spectroscopy, CHNS analysis, TGA, SEM, XRD spectroscopy, and various wet chemistry methods for the determination of cellulose, hemicellulose, lignin as well as physical properties such as the bulk density, surface negative charge and pH_{PZC} . The FTIR spectra showed peaks between $3200\text{--}3500\text{ cm}^{-1}$ attributed to OH group, $3000\text{--}2700\text{ cm}^{-1}$ assigned to --CH aliphatic stretch, and at about 1700 cm^{-1} assigned to O=C stretch, for all the adsorbents. This was indicative that all the *Macadamia* biosorbents consisted of a similar backbone structure. The changes that took place after chemical modification for the aforementioned organic functional groups for the RMN material was evidence that the different chemical treatments resulted in changes on the surface of the RMN material.

The differences observed in the percent lignin, cellulose, hemicellulose, carbon, hydrogen, nitrogen, and oxygen composition in all adsorbents was an indication that the surface changes were a result of the different chemical treatments. The modifications also affected the physical properties of the adsorbents such as the bulk density, surface charge, and the pH_{PZC} . The bulk density decreased as the surface area increased due to the extraction of soluble compounds. The pH_{PZC} of the materials increased upon treatment with the different chemical methods and the higher value of pH_{PZC} corresponded with the lower removal of Cr(VI) ions. Contrary, higher pH_{PZC} correlated with higher percent removal of Cd(II) , Co(II) ,

and Cu(II) by the RMN, AMM, and BMM materials. The modification of RMN with HCl resulted in a material with decreased surface negative charge whilst the NaOH modification produced materials with increased surface negative charge due to protonation and hydrolysis, respectively. After both the AMM and BMM materials were grafted with acrylic acid the surface negative charge decreased due to the increased concentration of carboxylate ion on the surface. The XRD patterns showed that the *Macadamia* based biosorbents consisted of a mixed morphology of both the amorphous and crystalline nature. The SEM images showed that the biosorbents consisted of layers of materials one on top of the other typical of plant materials and also, cavities that could have been involved in the adsorption of selected trace metals. The differences of the surface of the RMN after modification is evidence that the different chemical treatment methods gave rise to those surface changes. Whilst the similarities indicate that the treatment methods were not too severe such that it completely destroys the structural backbone of the RMN.

The RMN, AMM, and BMM materials demonstrated high affinity towards Cr(VI) ions with above 90% removed compared to 65%, 50%, and 45% for Cu(II) and the less than 30% for both Cd(II) and Co(II) removal for all the biosorbents. Therefore, only studies of Cr(VI) removal were dealt with in detail with all adsorbents. The optimal adsorption conditions obtained were pH 2, 100 mg/L initial concentration, 600 min of contact time, and 0.2 g adsorbent mass for the RMN, AMM, and BMM materials. For the 0.5 GAM and 0.5 GBM materials, the optimum conditions were pH 2, 180 min contact time, 25 mg/L initial concentration, and 0.15 g adsorbent mass. The optimum temperature was 40°C for all the biosorbents. The presence of competing ions did not influence the adsorption of Cr(VI) negatively in all the materials. NaOH was established to be a more appropriate Cr(VI) desorbing agent

than the HCl after Three consecutive desorption cycles. This demonstrated that the adsorbents may be used over extended cycles through regeneration. The adsorption isotherm data fitted the Langmuir model for the RMN, AMM, BMM, 0.5 GBM, and 0.5 GAM materials due to a higher r^2 values and maximum adsorption capacity suggestive of a homogeneous monolayer adsorption. The kinetic data were best described by the pseudo second-order model implying a chemisorption type process for all materials. The thermodynamic parameters for all the materials revealed that the adsorption process was spontaneous and endothermic. Overall, the results demonstrated that the *Macadamia* based biosorbents could be used for the adsorption of Cr(VI) ions from aqueous solutions since the *Macadamia* based biosorbents demonstrated a comparable adsorption capacity with other agricultural waste biosorbents. The adsorbents used in this study showed the ability to be regenerated as three cycles of desorption making the adsorbents an attractive prospect.

6.2 Recommendations

- To evaluate other modifying agents such as inorganic salts, organic solvents and to functionalize the biosorbents with amine compounds to try and improve the adsorption capacity of the adsorbents.
- To produce composite materials with superior adsorption properties than the pristine material.
- To evaluate the prepared adsorbents on real wastewater samples.
- To evaluate other desorbing agents like NaHCO_3 , Na_2CO_3 , etc.
- To characterize the biosorbents after adsorption with X-ray photoelectron spectroscopy (XPS) to determine the oxidation state of chromium on the adsorbent.

PRESENTATIONS ARISING FROM THIS DISSERTATION

- I. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E. Cr(VI) adsorption onto modified *Macadamia* nutshells and determination of the oxidation state of Cr after adsorption, 42nd National Convention of the South African Chemical Institute, 2015, 29 November to 4 December, Elangeni Hotel, Durban, South Africa, *Oral presentation*.
- II. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E. Characterization of raw and modified macadamia nutshell for removal of chromium, THE 17TH SOUTH AFRICAN CHEMICAL INSTITUTE INORGANIC CHEMISTRY CONFERENCE (INORG2015) incorporating the Carman Physical Chemistry Symposium, 2015, 28 June to 2 July, Rhodes University, Eden Grove Complex, Grahamstown, South Africa, *Poster presentation*.
- III. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E. Preparation of chemically modified *Macadamia* nutshell powder for adsorption of chromium(VI) from wastewater, Analitika, 2014, 7 to 11 September, Khaya iBhubesi, Parys South Africa, *Poster presentation*.
- IV. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E. Surface characterization of raw and modified *Macadamia* nutshells for the sequestration of Cr(VI) from wastewater, The 4th South African Young Water Professionals Biennial Conference and 1st African IWA Young Water Professionals Conference, 2015, 16 to 18 November, CSIR International Convention Centre, Pretoria, South Africa, *Poster presentation*.
- V. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E. Biosorption of hexavalent chromium from aqueous solutions by *Macadamia* nutshell powder, Center for Renewable Energy and Water Conference, 2016, 7 to 8 April, Vaal University of Technology

Southern Gauteng Science and Technology Park-Educity Campus Sebokeng, South Africa, *Oral presentation*.

- VI. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E, Cr(VI) adsorption unto acid and base modified *Macadamia* nutshells, International Conference on Environment, Materials, and green Technology, 2016, 24 to 25 November, Vaal University of Technology Southern Gauteng Science and Technology Park-Educity Campus Sebokeng, South Africa, *Oral presentation*.
- VII. Ntuli, T.D., Pakade, V.E., Ofomaja, A.E, Removal of Cr(VI) from aqueous solution by acrylic acid grafted *Macadamia* nutshells made easy, Vaal University of Technology 1st Interdisciplinary Research, Innovation and Postgraduate Conference 2016, 9 to 10 November, Vaal University of Technology Southern Gauteng Science and Technology Park-Educity Campus Sebokeng, South Africa, *Oral presentation*.

REPORTS ARISING FROM THIS DISSERTATION

Pakade, V. E., Ntuli, T. D. and Ofomaja, A. E. (2016) ‘Biosorption of hexavalent chromium from aqueous solutions by *Macadamia* nutshell powder’, *Applied Water Science*. Springer Berlin Heidelberg, 6, pp. 1–16.

Other reports

Pakade, V. E., Maremeni, L. C., Ntuli, T. D. and Tavengwa, N. T. (2016) ‘Application of quaternized activated carbon derived from *Macadamia* nutshells for the removal of hexavalent chromium from aqueous solutions’, *South African Journal of Chemistry*, 69, pp. 180–188.

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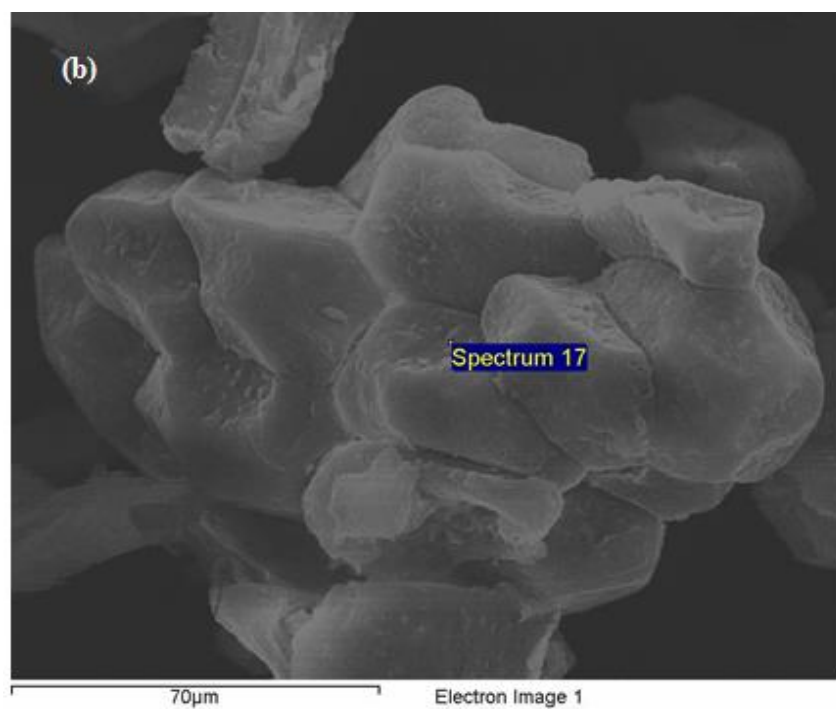
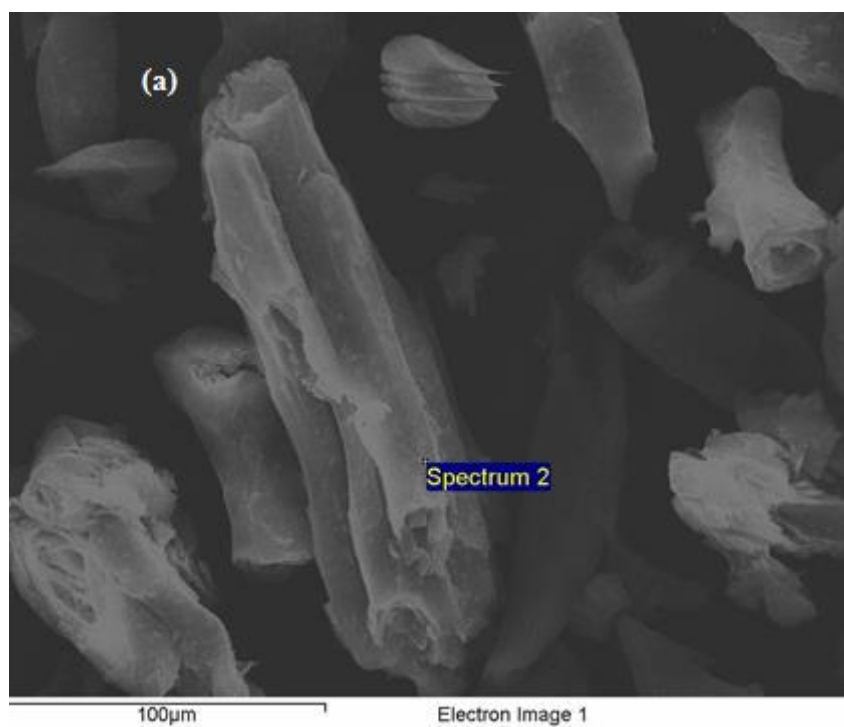
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**Appendix
Chapter 5.1**



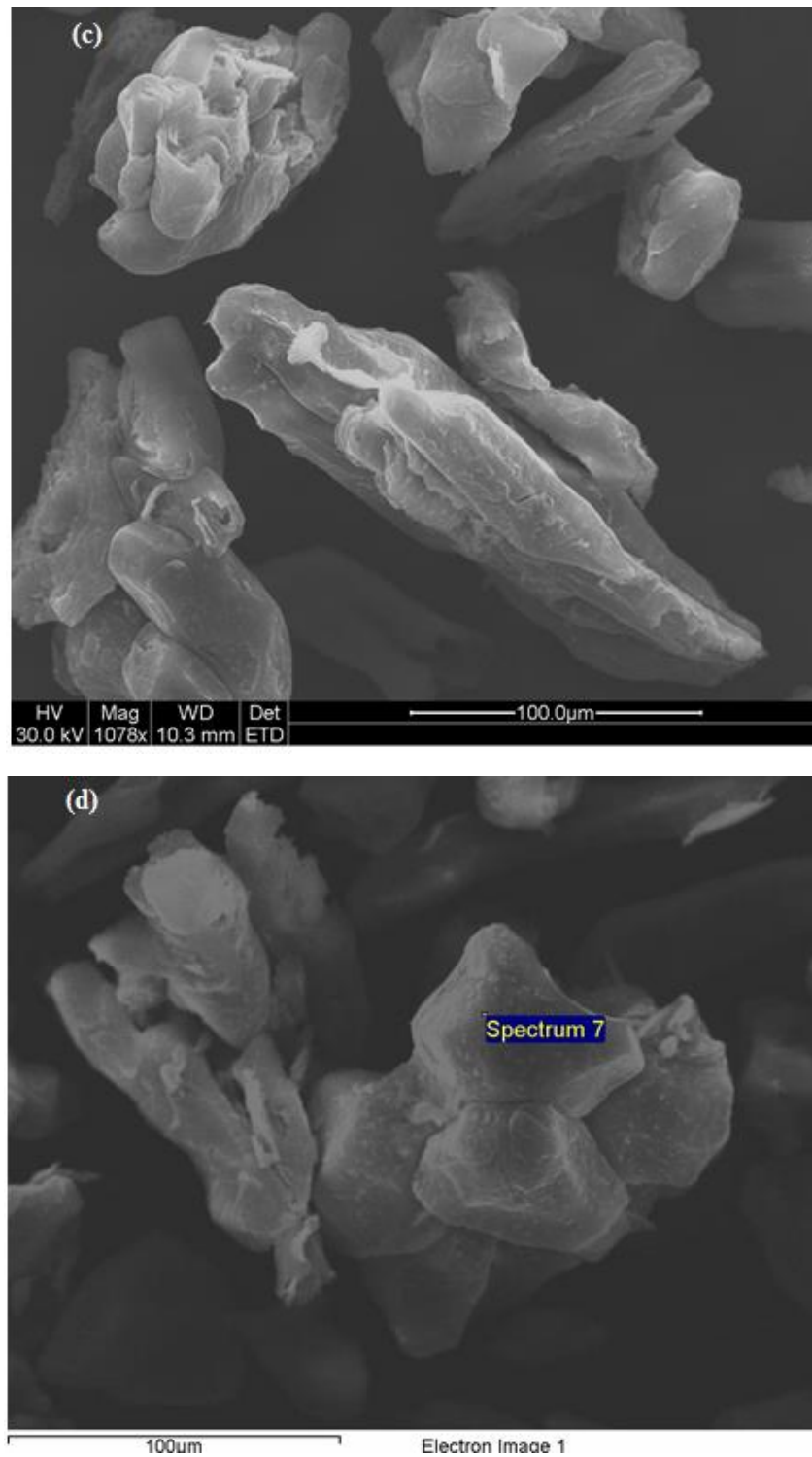
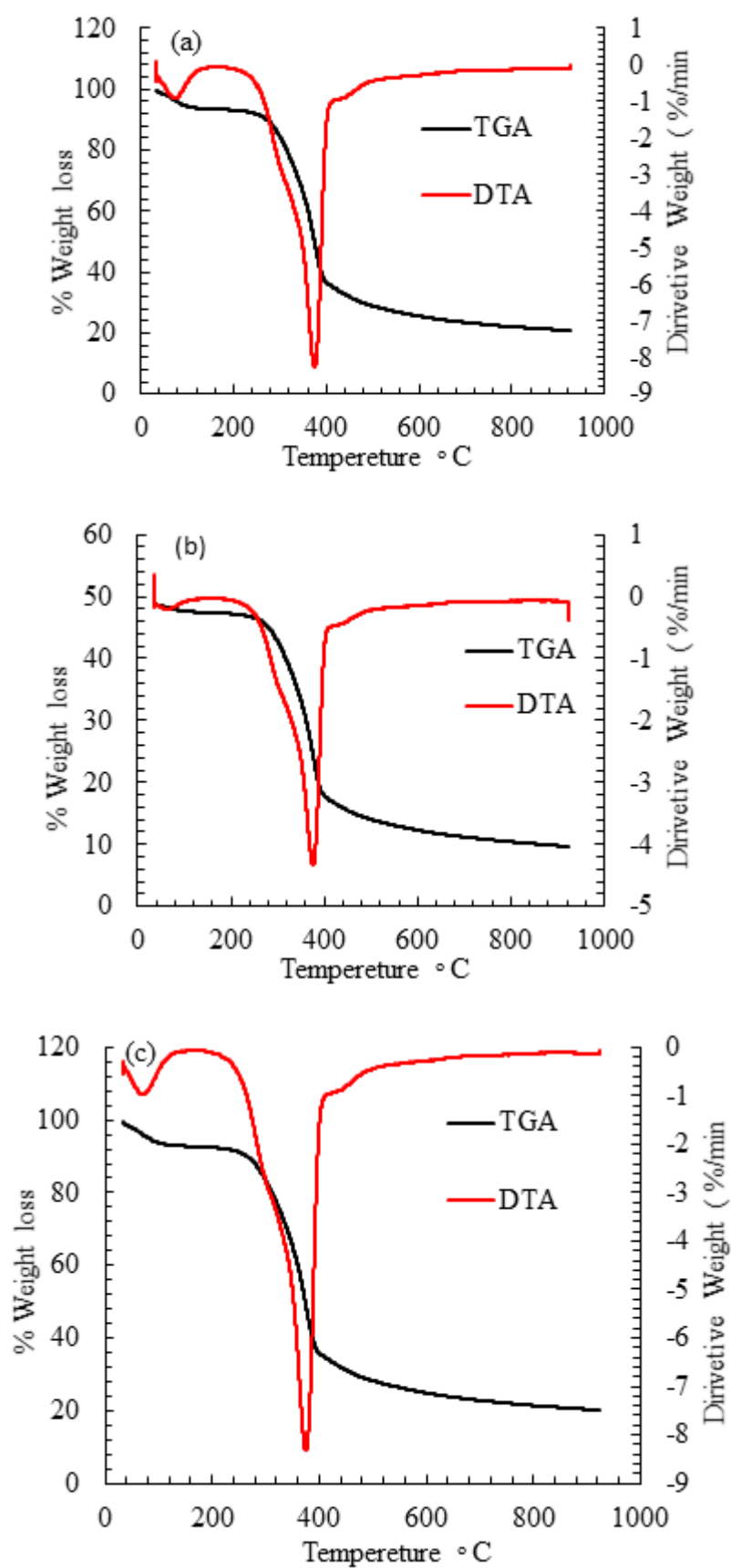


Figure A.1: SEM image for 1 GAM (a), 2 GAM (b), 1 GBM (c), 2 GBM (d)

Appendix 2

Chapter 5.1



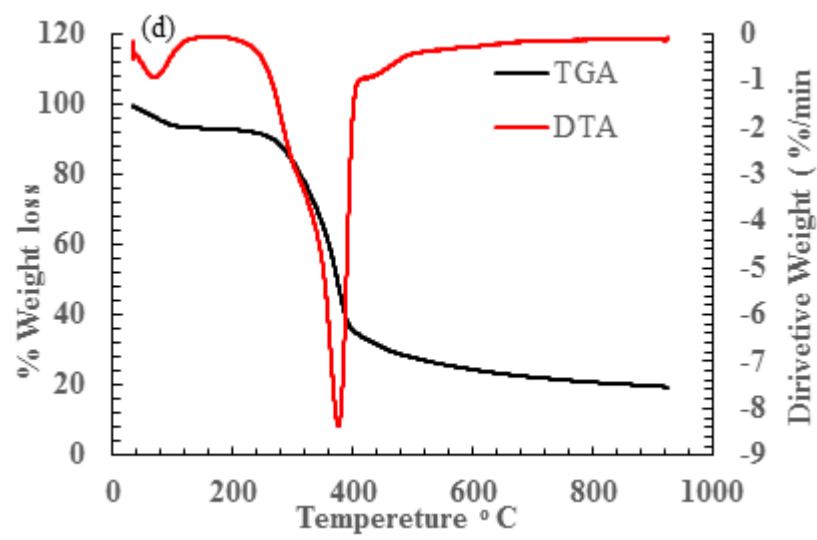


Figure A.2: TGA and DTA thermograms for 1 GAM (a), 2 GAM (b), 1 GBM (c), and 2 GBM (d) adsorbents.