



**Preparation, modification and characterization of
activated carbon derived from *Macadamia* nutshells and
its adsorption rate and capacity for $\text{Au}(\text{CN})_2^-$ compared to
commercially prepared coconut shells**

By

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Declaration

I, Refiloe Tsolele (undersigned), declare that the contents of this dissertation represent my own unaided work, and that the dissertation has not previously been submitted in part, or in whole, to any other university. Where use has been made of the work of others, it has been duly acknowledged in the text.

Signature: 

Date: 22/03/2018

ABSTRACT

Activated carbons have been produced from various carbonaceous source materials including nutshells, peat, wood, coir, lignite, coal and petroleum pitch and the produced carbons have been used for adsorption of inorganic and organic compounds from numerous matrices. Activated carbons are characterized by large surface area and high degree of microporosity. The ability of activated carbon to adsorb gold from solutions, which is present in very low concentrations while loading to fairly high concentrations, has made it an attractive material for the concentration of gold from dilute solutions. Consequently, the use of activated carbons for the recovery of gold from cyanide-leached liquors has gained wide acceptance in the mining industry. However, the price of commercially prepared carbons, the time taken for them to arrive, the breakage of the carbon during transportation and the interest in utilization of various local wastes for the generation of adsorbents has led to a search of more cost effective and time friendly source for the activated carbons.

The focus of this research was to conduct a study in which a comparison was conducted between untreated coconut shell derived activated carbon (CAC) and Macadamia nutshell derived activated carbon (MAC) for the adsorption of gold. These activated carbons were modified with HNO_3 and H_3PO_4 to increase their surface adsorption properties. This was done in order to explore if these activated carbons prepared from Macadamia shells could be an attractive alternative or a complementary supplement to the coconut shell based carbons that are currently being used in the gold extraction industry. The modification of the commercially prepared Macadamia activated carbons was done with 3 different concentrations for both nitric acid and phosphoric acid. The modified activated carbons were labelled $\text{MACP}_{20\%}$, $\text{MACP}_{40\%}$ and $\text{MACP}_{60\%}$, to signify the materials prepared from 20% (v/v) H_3PO_4 , 40% (v/v) H_3PO_4 and 60% (v/v) H_3PO_4 , respectively. Same labelling was used for 20% (v/v) HNO_3 , 40% (v/v) HNO_3 and 55% (v/v) HNO_3 modifications to correspond to $\text{MACN}_{20\%}$, $\text{MACN}_{40\%}$ and $\text{MACN}_{55\%}$, respectively. Also, untreated coconut shell derived activated carbon (CAC) and Macadamia nutshell derived activated carbon (MAC) were investigated for gold adsorption for comparison purposes. All the activated carbons prepared in the

study were characterized with Brunauer-Emmet-Teller (BET), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA), elemental analysis (EL) and X-ray diffraction spectroscopy (XRD). The physical properties of the activated carbons were done by determining attrition, ash content, volatile matter, and moisture content of all the activated carbons. Various parameters that affect selective adsorption such as the effect of initial concentration, time, agitation speed, interfering species, and dose of the adsorbent were investigated. Optimal parameters for gold ion adsorption were as follows: solution pH, 10; contact time, 6 h; agitation speed 150 rpm; sorbent amount 4 g and 5.5 ppm for initial concentration of gold. The observed selectivity order was not the same for all the adsorbents but the adsorption of gold was found to be mostly influenced by the presence of nickel and least influenced by copper. The MACP_{60%} was found to be the most effective from the three concentrations investigated for the phosphoric acid modified activated carbons yet proved to have lower adsorption capabilities compared to CAC. The MACN_{55%} was found to be the most efficient and displayed similar adsorption capabilities to those of CAC.

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GLOSSARY OF ABBREVIATIONS

AC	Activated Carbon
ACF	Activated Carbon Fibers
BET	Brunauer Emmett Teller
CAC	Coconut activated carbon
FAO	Food and Agricultural Organisation
FTIR	Fourier Transform Infrared spectroscopy
GAC	Granular activated carbon
KF	is the Freundlich constant
MAC	<i>Macadamia</i> activated carbon
MACN _{20%}	MAC modified by 20% (v/v) nitric acid solution
MACN _{40%}	MAC modified by 40% (v/v) nitric acid solution
MACN _{55%}	MAC modified by 55% (v/v) nitric acid solution
MACP _{20%}	MAC modified by 20% (v/v) phosphoric acid solution
MACP _{40%}	MAC modified by 40% (v/v) phosphoric acid solution
MACP _{60%}	MAC modified by 60% (v/v) phosphoric acid solution
n	is the Freundlich exponent
PAC	Powdered activated carbon

SEM	Scanning Electron Microscope
El	Elemental analysis
TGA	Thermo-Gravimetric Analysis
XRD	X-Ray diffraction spectroscopy

Dedication

To the Soul that has opened my heart to love again, our new addition to the family, Reabetsoe Tsolele, your arrival to this world has made me extremely happy. This thesis is proof that your dreams are valid little one!

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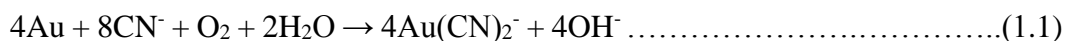
CHAPTER 1: INTRODUCTION

1.1 Background on the removal of gold

It is estimated that two thirds of the gold mined worldwide comes from South Africa, whilst the rest comes from Australia and North America (Dreisinger and Molleman, 2002). However, during processing some gold is lost through the waste streams. This has led to a demand for the development of more techniques and adsorbents to be used for effective or efficient recovery of gold. Various processes have been used for the recovery of gold from ore following some sort of extraction. These included chemical, physical or surface based processes in which each process relies on the initial grinding of the ore (Hylander, 2007). The most widely used methods in hydraulic metallurgy are amalgamation with mercury, chlorination, and cyanidation (Dreisinger and Molleman, 2002). Recovery by amalgamation has declined steadily due to its hazardous and toxic nature (Hylander, 2007). Inhalation of mercury can disrupt the nervous system, damage the brain functions and trigger allergic reactions such as rashes, tiredness, and headaches (Hylander, 2007). Attempts to improve recovery using chlorination proved costly and ineffective due to the excessively high reagent consumption of the process (Van den Berg, 2000).

Owing to the above-mentioned drawbacks, the bulk of the world's gold production is now recovered by the cyanidation process (Eugene and Mujumdar, 2009). The cyanidation process was introduced by MacArthur and the Forrest brothers of Glasgow in the 1890's (Dreisinger and Molleman, 2002). The process involves the dissolution of the gold in aqueous alkaline cyanide solution and subsequent

separation of the gold bearing solution from the finely ground ore (Kondos *et al.*,1995). The process has been used to treat ores, concentrates and calcines on a commercial scale all over the world. The cyanidation process occurs in an alkaline solution and it is an oxidative leaching process, *i.e.* oxygen is required for the reaction to occur. Atmospheric oxygen is usually adequate. The overall reaction between gold and cyanide can be expressed as follows (McCracken, 1993):



The aurocyanide ion formed is a very stable linear complex. The reaction can be divided into (i) the anodic dissolution of gold which is expressed as follows:

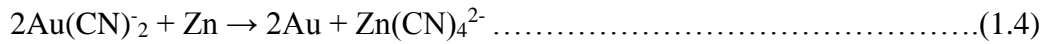


and (ii) the reduction of oxygen which is the cathodic reaction is expressed as follows:



The cyanidation process is preferred over other methods due to it being less expensive, simple, and superior selectivity towards gold (Eugene and Mujumdar, 2009). After leaching the gold ores and concentrates with cyanide, a pregnant solution of anionic metal cyanide complexes is obtained from which gold must be recovered. The aurocyanide complexes, which have formed, may be removed by one of the following processes: zinc cementation; removal by ion-exchange resin and adsorption onto activated carbon in the carbon-in-pulp process. Zinc precipitation or cementation was patented by MacArthur *et al.* (1890) at the same time, the author patented cyanidation as an extraction technique. The process has been improved and redeveloped over the years and has now become what is known

as the Merrill-Crowe process (Marsden and House, 2006). Its recovery may be represented by the following reaction:



The technique involves addition of fine zinc dust into a pregnant leach solution. The pregnant cyanide solution from the clarification process is added separately to the frame filters. Zinc dust and lead nitrate are then added to the clarified cyanide solution to precipitate the gold. The de-aeration tanks allow dissolved oxygen in the pregnant solution to be filtered just before the addition of the zinc dust. The oxygen is removed because it causes increased zinc consumption (Nicol *et al.*, 1984, Das *et al.*, 1996). The zinc-gold precipitate is then smelted to separate the gold from the zinc. The emulsion formed is pumped through a filter system and the gold zinc slime is then filtered from solution. The barren filtrate is recycled for further extraction of gold. Although Merrill-Crowe process using zinc-cementation proved to be of great efficiency considering the low gold residue of the solutions, many disadvantages have been associated with the process.

Cementation is known to be sensitive to alkalinity and to the concentration of free cyanide in solution (Nicol *et al.*, 1984, Das *et al.*, 1996). Another reason was that many of the more common constituents of gold-cyanidation solutions influence the cementation reaction which led to the decrease in cementation and hence gold recovery (Nicol *et al.*, 1984, Das *et al.*, 1996). Due to this the Merrill-Crowe process as currently practiced in South Africa requires very careful control and at the same time, it is a relatively a labor-intensive operation (Marsden and House, 2006). The use of an ion-exchange resin for the recovery of gold from cyanide pulp was first proposed in South Africa in 1960 by Davidson and pilot-plant tests were

carried out at that same time. The earlier development of resin-in-pulp for gold extraction using an anion exchange resin came from the Soviet Union (Kondos *et al.*, 1995). The use of ion-exchange resin as an alternative to activated carbon for the recovery of gold process is currently being examined as a possible alternative to the carbon-in-pulp process. Resin-in-pulp has proven to have several advantages (Kondos *et al.*, 1995) over activated carbon (AC), such as its ability to be effectively eluted at room temperature, whereas the elution of activated carbon has to be carried out at higher temperatures and pressure. However, there are two major problems with ion-exchange resins which have led to them not being utilized much in the mining industry. Ion-exchange resins are less selective compared to AC for gold cyanide over the base metal cyanides. The resin particle size is smaller, which presents problems associated with the separation, transportation and mixing of the resin in pulp mixture (Eugene, 2009). As a result, gold is mainly being recovered from these solutions using adsorption onto AC.

A patent detailing a metallurgical process for the recovery of gold by charcoal from leach liquors in was published way back in 1880 (Eugene, 2009). Its initial success was restricted by the low surface area, low abrasive strength of early carbons and also by the lack of a suitable procedure for elution of gold from the loaded carbon (Das *et al.*, 1996). ACs were used for the recovery of gold from slimy ores, which were difficult to treat using conventional Merrill-Crowe techniques due to the filtration and clarification difficulties (Fraser and Wells, 1991). The rapid development of carbon recovery systems in recent times can be accredited to the work of Zadra *et al* (1952) in developing a process for the recovery of gold and silver from activated carbon by leaching and electrolysis. Zadra *et al.* (1952) also developed high surface area and abrasion resistant carbon products (McCracken,

1993). Consequently, ACs for gold recovery from cyanide-leached liquors has gained wide acceptance in the mining industry (Soleimani, 2007).

1.2 Purpose of study

In this study activated carbons produced from *Macadamia* nut-shells were compared to the activated carbons sourced from coconut shells on their adsorption of gold cyanide ion from gold solution. *Macadamia* based activated carbons have a high cracking pressure making them resistant to attrition which is an important characteristic in metallurgical plants. However, the relative adsorption capacities of *Macadamia* based ACs are usually low. The focus of this research was to conduct a study in which activated carbons prepared from waste *Macadamia* nut-shells were investigated in the recovery of gold. These ACs were modified by HNO_3 and H_3PO_4 to improve their adsorption properties. This was done in order to explore if the modified ACs prepared from *Macadamia* nut-shells could be an attractive alternative or a complementary supplement to the coconut shell based ACs currently being used in the gold extraction industry.

1.3 Justification of Study

The use of ACs for gold recovery from cyanide-leached liquors has gained worldwide acceptance in the mining industry. However, only ACs prepared commercially from coconut shells are presently used in the gold processing plants. These commercially prepared ACs are currently being imported to South Africa from other countries. The price is extremely high and this has led to a search for more cost-effective activated carbons. *Macadamia* nut plantations are becoming an important crop in South Africa and are possibly the fastest growing tree crop industry in the country (Mogale, 2012). Enormous amounts of *Macadamia* nut-

shell are generated every year after processing *Macadamia* nut in food industries such as oil factories and confectionery. According to a report from the Department of Agriculture, Forestry and Fisheries, South Africa produced almost 30000 tons of *Macadamia* nuts in 2012 (DAFF, 2012). This translates to thousands of tons of waste nutshells. An efficient waste management in this area is of high importance as it can contribute to the reduction in disposal costs, as well as offering environmental advantages. Furthermore, innovative waste management might lead to the production of a valuable product with possible added value which mitigate waste management costs or possibly even offer a financial return adding to the increase in the country's economy and a cut of costs in the mining sector, which will decrease financial strain and lead to saving costs. Studies (Poinern *et al.*, 2011, Pezoti *et al.*, 2014) have shown that *Macadamia* nut-shells can produce a high quality granular activated carbon (GAC) adsorbent and this study was aimed at investigating if it can be utilized by the mining industry.

However, to be effective the ACs that are produced must be resistant to attrition and transportation within the system because fine AC is undesirable in the mining industry as it will lead to loss of adsorbed Au through the screens (Yalcin and Arol, 2002). *Macadamia* nutshells have a high cracking pressure, a property which is attractive for producing high quality ACs that are resistant to attrition. Poinern *et al.* (2011) compared *Macadamia* and coconut shell-based ACs for the recovery of gold cyanide ion. However, to the best of the author's knowledge, no study has been reported on the use of H₃PO₄ and HNO₃ modified MAC for the recovery of gold from mining liquors. The ACs were modified with different concentrations of HNO₃ and H₃PO₄ to improve their adsorption properties. This was done in order

to explore if the modified ACs prepared from *Macadamia* nut-shells could be an alternative low-cost adsorbent for the extraction of gold ions in aqueous solutions.

It has been further stated that the concentration of the activating agent used for modification influence the final properties of ACs like pore structure, pore volume, surface area and the density of oxygenated functional groups (Yavuz et al., 2014). But sometimes secondary modification can lead to obliteration and total disintegration of ACs internal structure. Therefore, it is paramount to investigate the optimum concentrations of activating agents needed for improved performance. Thus, the focus of this research was to conduct a study in which ACs prepared from waste *Macadamia* nut-shells were investigated in the recovery of gold. The ACs were modified with different concentrations of HNO_3 and H_3PO_4 to improve their adsorption properties. This was done in order to explore if the modified ACs prepared from *Macadamia* nut-shells could be an alternative low-cost adsorbent for the extraction of gold ions in aqueous solutions.

CHAPTER 2: LITERATURE REVIEW

2.1 Definition of activated carbon

Balcı *et al.* (1992) described AC as a microcrystalline form of carbon with a very high porosity and surface area. It was also stated that AC may be visualized as a form of solid that has a large surface area within a rigid granule or particle structure of relatively small volume. According to Benaddi (2000) AC is predominantly an adsorbent with a large internal pore volume and surface area. Kilic *et al.* (2012), on the other hand, described AC as a form of carbon that is composed of a group of materials including a wide range of carbaceous materials known for its small sized pores and high surface area that ranges from 100-1500 m²/g.

AC has become one of the most technically important and widely used adsorbents due to its high adsorptive capacity which is related to the properties such as surface area, pore volume and pore size distribution (PSD). In the last decades, activated carbon acquired much attention in different technologies, especially in adsorption processes (Williams and Reed, 2006). Also, AC is stable to light, heat and many oxidizing agents because of its complex molecular structures (Khambhaty *et al.*, 2012). Large scale productions of AC with appropriate characteristics for each particular application is in demand due to recent technologies in various industries. In general, the desired properties of AC applications are, it must have adequate adsorptive capacity, chemical purity, and mechanical strength. Literature survey shows that there have been many attempts to obtain low-cost activated carbons from agricultural wastes such as coconut shells, wood (Gomez-Serrano *et al.*, 2005; Klijanienko *et al.*, 2008; Zuo *et al.*, 2009), cotton stalk (Deng *et al.*, 2010), almond shells (Bansode *et al.*, 2003), rice husk (Fierro *et al.*, 2010; Guo and Rockstraw,

2007), date pits (Girgis and El-Hendawy, 2002), nut shells (Lua *et al.*, 2005; Yang and Lua, 2006), olive seeds (Stavropoulos and Zabaniotou, 2005), apricot stones (Youssef *et al.*, 2005), and sugar cane bagasse (Cronje *et al.*, 2011; Valix *et al.*, 2004). Due to the increasing demand of AC, there is a strong need for sourcing out new precursors for the preparation of AC which must be cost-effective and at par with the commercially available AC. Although, a variety of raw materials were explored for the preparation of AC in earlier studies, scientists are still trying to explore new materials depending on their availability and suitability for AC production in the recovery of gold. Hence, there was a need for this study, to determine if AC derived from *Macadamia* nut-shells could be used to replace the commercial AC derived from coconut shells for application in mining industry effluents.

2.2 Preparation of activated carbons

Initially, AC was produced using either steam or chemical activation, both of which required the use of elevated temperatures. Some researchers have studied the effect of combined or consecutive physical and chemical activation and reported enhanced results (Rodriguez-Reinoso *et al.*, 1982; Caturla *et al.*, 1991; Ansari and Omidvari, 2005). In general, chemical activation is sometimes favorable due to the lower activation temperature and time, and well-developed porosity that result in the activated carbons. The basic production processes can be combined in different ways. Sometimes the chemically activated carbon is subjected to additional activation with a gaseous environment or microwave technique in order to change the pore structure of the final product (Sharifan, 2013). In the following subsections carbonization, activation, chemical activation, steam activation and modification will be discussed.

2.2.1 Carbonization

Carbonization is the process in which carbon-rich material is converted into carbon char by heating at high temperatures (up to 800°C) in the absence of oxygen. The term carbonization has been historically used to describe a form of slow pyrolysis with the objective of producing char as the main end-product, whilst pyrolysis generally refers to higher heating rates to produce gases and pyrolytic liquids rather than char. Syn-gas and bio-liquids are also formed besides the main solid product through carbonization, and have been suggested as a means of maintaining the thermal process (Strezov *et al.*, 2007). Elemental carbon as a solid residue with a proto-graphitic structure, called elementary crystallites is retained during carbonization when almost all non-carbon elements including oxygen, hydrogen, nitrogen and sulphur are eliminated in the form of volatiles. A typical lignocellulose material exhibits a chemical composition of 48 wt% carbon, 6 wt% hydrogen and 45 wt% oxygen.

The degree of conversion to char varies as a function of the amount of carbon being removed with O and H in the form of carbon oxides and hydrocarbons (Marsh and Rodriguez-Reinoso, 2006). The char yield from biomass has been thermo-chemically determined and found to be around 27% for carbonization of cellulose at 400°C, and this is assumed to be the char yield limit. This is due to the fact that char yields from other biomass are not just pure cellulose (Antal and Gronli, 2003). Although the mechanism of carbonization has been found to be complicated it can be simplified into three consecutive steps. The initial step at temperatures around 300°C involves the loss of moisture and some light volatiles. The primary formation of char takes place in the second step, at temperature of 500°C in which liquid fraction evolution occurs at its highest rate. Primary carbonization step is

also related basically to the decomposition of cellulosic compounds accompanied by the formation of carbon oxides at the highest rate. Secondary carbonization takes place in the third step at higher temperatures (400-700°C) following the primary de-volatilization. This step involves cracking, polymerization, and re-condensation of liquid fraction and slow condensation of the char structure to form a carbon rich solid residue. The main product of the secondary de-volatilization involves the cracking of liquid compounds which are complex hydrocarbons. They are highly detected at temperatures below 600°C, while the dominant reaction which occurs at temperatures over 600°C is the condensation of carbon char with evolution of hydrogen and CO (Strezov *et al.*, 2007). The final product of carbonization is the porous structure formed from randomly cross-linked flat aromatic sheets. The pore structure at this stage is however not yet highly developed, since normally it is partly filled with tarry materials, the product of secondary reactions and the disorganized aromatic sheets. Due to this, the char produced at this stage has generally a low adsorptive capacity (Strezov *et al.*, 2007). Therefore, a further activation stage is usually required to improve the porosity of activated carbons.

2.2.2 Activation

The activation process helps to increase the porosity of the charred material. The properties of the activated carbon are to a great extent related to the activation method, as well as the characteristics of raw materials. A well-developed porous structure can be produced through appropriate activation; as an example of correct activation, scanning electron microscopy (SEM) images of carbonized and activated char from coconut shells from an optimization study by Tan *et al.* (2008) are shown in Figure 2.1.

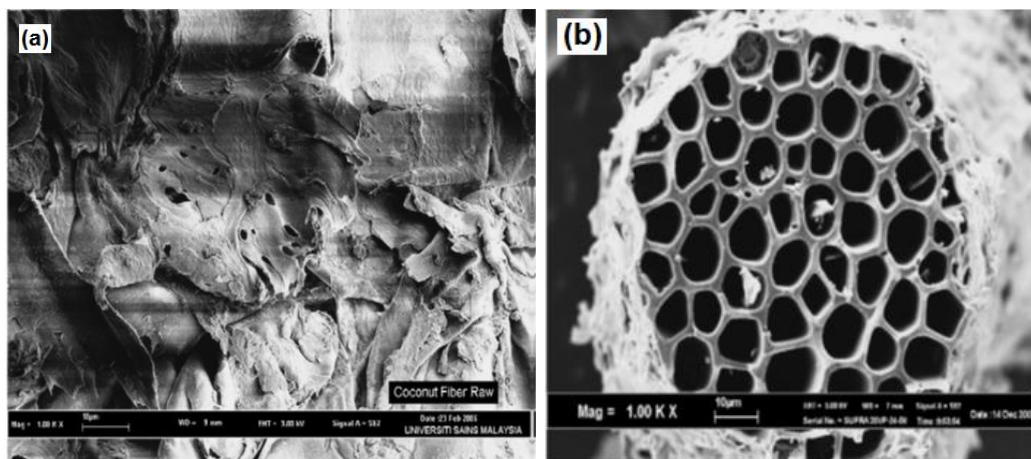


Figure 2.1 SEM images of a) carbonized coconut shells b) activated carbon from coconut shells (Tan *et al.*, 2008): Scale 10 µm.

Activation reaction starts with opening of the blocked pores and removal of the disorganised carbon produced during carbonisation. The process progresses with the exposure of aromatic sheets to the activating agent and further enhancement of the porous structure. This usually result in the formation of micropores, followed by widening of existing pores and creation of large size pores through burning away the walls between the adjacent pores. At this stage, the extent to which carbon is burnt off is indicative of activation degree (Tan *et al.*, 2008). Generally, activated carbon is manufactured by two essential activation methods, including physical (thermal) activation and chemical activation as shown in Figure 2.2 (Suhas *et al.*, 2009). The characteristics of activated carbon involve; pore size distribution, shapes of the pores and surface chemistry which effectively depends on the nature of carbonaceous precursor, activation methods and activation conditions (Kong *et al.*, 2013).

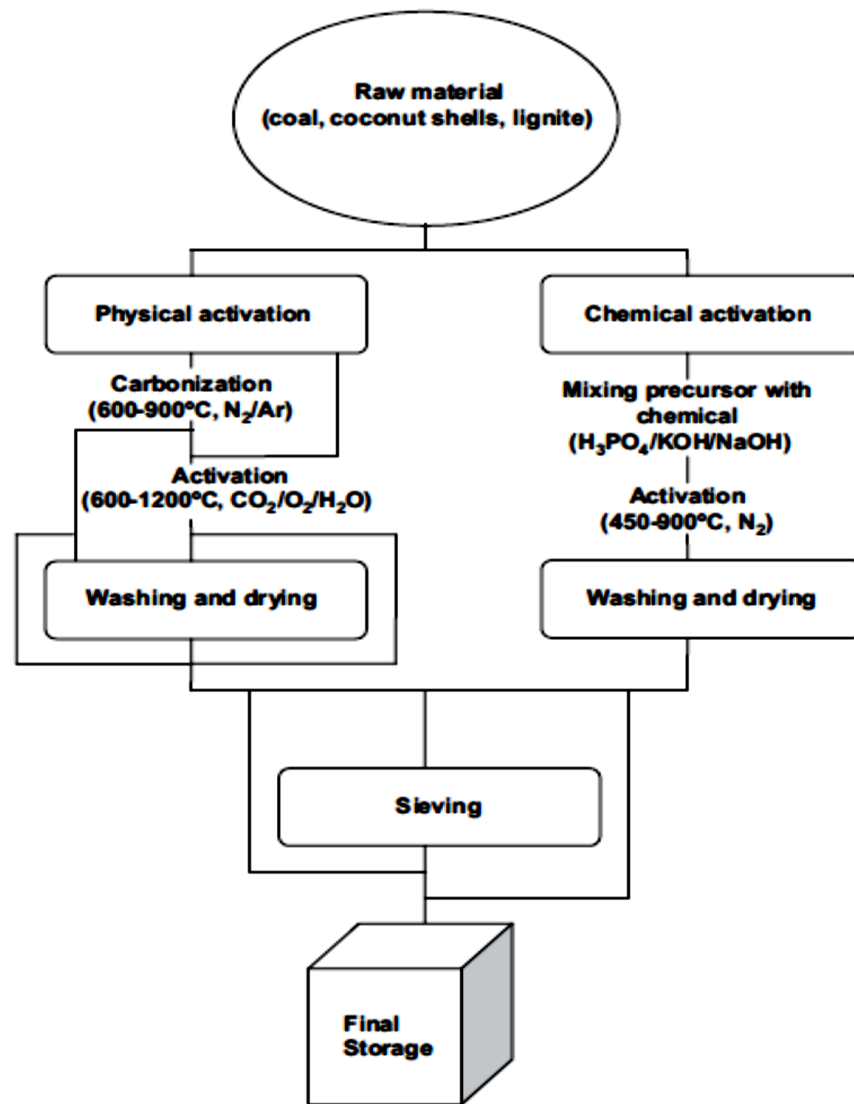


Figure 2.2: Schematic diagram of the production process of activated carbons (Suhas *et al.*, 2009).

2.2.3 Physical Activation

Physical activation is one of the activation methods that play a significant role in the production of activated carbon especially in the determination of the size and effectiveness of the pores. Various methods have been developed for physical activation but they all share the same basic principle. First the material undergoes initial carbonization at 500-600°C, followed by activation with steam at 800-1100°C (Mohamad Nor *et al.*, 2013).

a) Carbonization

During carbonization phase, carbon content of the product attains a value of about 80 percent. At the carbonization stage most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material and the freed atoms of elementary carbon are grouped into organized crystallographic formation known as elementary graphitic crystallites (Nabais *et al.*, 2013). The main aim of carbonization is to reduce the volatile content of the source material in order to convert it to a suitable form for activation. The carbon material is usually carbonized at 500-600°C with a dehydrating agent like zinc chloride, sulphuric acid or phosphoric acid for an example.

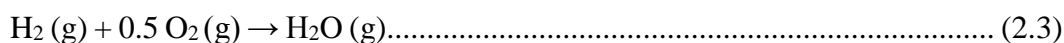
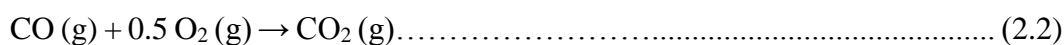
b) Activation of carbonized intermediate product with gaseous agents

The most common activation agents are steam, carbon dioxide and oxygen (air). The activation step is generally conducted at temperatures between 800°C and 1100°C. The active oxygen in the activating agent basically burns away the more reactive portion of the carbon skeleton as carbon monoxide and carbon dioxide, depending on the gaseous agent employed.

The char then reacts with steam for one hour to produce activated carbon. At this point, the char consists entirely of elemental carbon, and some of the carbon reacts with water to produce carbon monoxide and hydrogen gas. The gas escapes from the solid char, leaving behind pores in the carbon solid (Hung, 2012). The endothermic carbon-steam reaction takes place in the furnace according to the following reaction:



The carbon monoxide and hydrogen gases auto-combust to form water and carbon dioxide gas as depicted by the exothermic reaction 2.2 and 2.3:



After the exothermic reaction, has taken place, the activated carbon is cooled and packaged for use (Gottipati 2012). Studies of physical activation are showed below in Table 2.1. where various advantage agents were used on numerous precursors to produce ACs for different purposes.

Table 2.1. Various physical activating agents and precursors used for AC production (adapted from Gottipati 2012)

Activating agent	Precursor	References
Stream	Hazel-nut	Haykiri-Acma <i>et al.</i> , 2006
	Sunflower shells	Lazaro <i>et al.</i> , 2007
	Novel biomass	Nabais <i>et al.</i> , 2008
	Fly ash	Lu <i>et al.</i> , 2010
	Rice husk	Zhang <i>et al.</i> , 2011
CO ₂	Coffee endocarp	Nabais <i>et al.</i> , 2008
	Corn cob	Aworn <i>et al.</i> , 2009
	Waste tyre	Betancur <i>et al.</i> , 2009
	Pecan shells	Salvador <i>et al.</i> , 2009
Air	Almond tree bark	Ganan <i>et al.</i> , 2006
	Pitch-based	Liu <i>et al.</i> , 2007
	Olive tree wood	Ould-Driss <i>et al.</i> , 2011

2.2.4 Chemical Activation

Preparation of ACs by chemical activation is a single step process in which carbonization and activation are carried out simultaneously (Gottipati, 2012). Rich

carbon content materials are produced as a result of the pyrolysis process with high porosity structure. Chemical agents such as H_3PO_4 , HCl , HNO_3 , ZnCl_2 , KOH , NaOH , K_2CO_3 and Na_2CO_3 can be used in chemical activation (Kilic *et al.*, 2012; Olorundare *et al.*, 2012). The advantages of chemical activation over physical activation include low energy, less cost of the activation process and better porous structure characteristics of the product.

Table 2.2 Various chemical activating agents and precursors used for AC production (Gottipati, 2012)

Activating agents	Precursors	References
ZnCl_2	Cattle manure	Qian <i>et al.</i> , 2007
	Tamarind wood	Acharya <i>et al.</i> , 2009
	Tamarind wood	Sahu <i>et al.</i> , 2010
	Biomass	Liou, 2010
	Sugarcane	Cronje <i>et al.</i> , 2011
KOH	Petroleum coke	Kawano <i>et al.</i> , 2008
	Cotton stalk	Tseng <i>et al.</i> , 2008
	Rice straw	Basta <i>et al.</i> , 2009
	Coal	Wu <i>et al.</i> , 2010
	Pineapple peel	Foo <i>et al.</i> , 2011
K_2CO_3	Walnut shell	Hayashi <i>et al.</i> , 2002
	Palm shell	Adinata <i>et al.</i> , 2007
	Bamboo	Horikawa <i>et al.</i> , 2010
	Pineapple peel	Foo <i>et al.</i> , 2011

In addition, the chemical activation product has a large surface area and higher carbon yields due to prevention of formation of volatile compounds and tar because of the dehydrogenation properties of the chemical agents (Williams *et al.*, 2004). Chemical activation process requires the washing stage to remove the impurities coming from the chemical agent that may affect the properties of activated carbon.

Another disadvantage is the corrosiveness of the process (Yeganeh *et al.*, 2006). Moreover, the yields of carbon in chemical activation are usually higher than those in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of other volatile products. Numerous studies have reported the preparation of ACs by chemical activation for various applications (Table 2.2). However, a secondary chemical treatment of ACs is sometimes necessary in order to modify or improve surface properties.

2.2.5 Modification of activated carbon

The type and amount of chemical functional groups on the AC surface can be changed with surface modification methods such as chemical impregnation, physical, and microwave treatments (Valdes, 2002). Depending on the nature of the reagent used in modification, either positively or negatively charged functional sites can be formed on the surface which transforms AC to a more hydrophilic or hydrophobic and acidic or basic character. Modification and impregnation techniques increase surface adsorption and removal capacity as well as improve the selectivity of analyte adsorption (Monser and Adhoum, 2002). Chemical surface modification methods are widely used to prepare hydrophilic AC. Hydrophilicity of AC is associated essentially with the presence of oxygen containing groups on the surface such as carboxyl, phenolic and lactonic groups. Nitric acid, sulphuric acid, phosphoric acid hydrogen peroxide, ozone and potassium permanganate are some of the reagents frequently used to enhance oxygen content on the surface of AC (Yin, 2007). It has been demonstrated that the amount of oxygen containing surface functional groups, specific surface area and pore structure highly depend on the concentration of reagents (Wang *et al.*, 2011). While oxygen content of AC

usually increases with the increase of reagent concentration, the surface area and pore volume values decrease adversely (Valdes, 2002).

Therefore, modification conditions must be well defined in terms of surface chemistry and textural characteristics because most of the applications of AC are highly connected to these properties. Metal adsorption depends on cation exchange mechanism between metal ions and acidic surface functional groups formed on the AC surface. It has been stated in the literature that acid modified AC shows good chelation ability with metal species while their organic pollutant adsorption performances decrease with acid interaction (Wang, 2006). The benefits of using chemical treatment are the low temperature needed in the process, and shorter treatment time. Only one single step is needed, and the global yield is greater because the burn-off char is not required (Budinova *et al.*, 2006). Examples of chemical modification of ACs using H_3PO_4 and HNO_3 are illustrated in Table 2.5.

Table 2.3 Table showing previous studies on modification of activated carbons using H_3PO_4 and HNO_3 (modified from Gottipati 2012)

Activating agent	Precursor	References
H_3PO_4	Almond shell	Zuo <i>et al.</i> , 2009
	Cotton stalk	Deng <i>et al.</i> , 2010
	Rice straw	Fierro <i>et al.</i> , 2010
	Sewage sludge	Wang <i>et al.</i> , 2011
	Pineapple leaf	Mopoung <i>et al.</i> , 2015
HNO_3	Olive-stones	Youssef <i>et al.</i> , 2006
	Coconut shells	Vasu 2008
	Waste tea	Yavuz <i>et al.</i> 2014
	Commercial carbons	Lopes <i>et al.</i> ,2015

In the present study, the company in which *Macadamia* ACs were sourced from is Filtatech Activated Carbon Innovations (Boksburg, South Africa) and were prepared by physical activation of *Macadamia* nutshells. The ACs were chemically modified by impregnating the carbons with nitric and phosphoric acid to improve the adsorption properties of *Macadamia* ACs. The *Macadamia* activated carbon are hard, pure and resistant to attrition, however they have low adsorption capacity. As a result, this study was done to see if modification with nitric and phosphoric acid can improve their adsorption capacity and hence be a complimentary source of activated carbon in the mining industry which currently uses activated carbons sourced from coconut shells.

2.3 Factors affecting ACs quality

The quality of the resulting activated carbon is influenced by the raw material used, concentration of the activating agent, temperature, particularly the final activation temperature which affects the characteristic of the activated carbon produced and the activation time which also affects the carbonization process and properties of activated carbon.

2.3.1 Raw material

Activated carbon has an immense worldwide market of about 1,000,000 tonnes per year (Sharifan, 2013). Preferably, the raw material should be from a nearby source to reduce the cost of transportation and not require cyclic cropping procedure (Marsh and Rodriguez-Reinoso, 2006), have high carbon content, low in inorganic content (*i.e* low ash), high density and sufficient volatile content, cellulosic and lignocellulosic waste, available in large quantities, especially from agricultural operations such as fruit stones and various nutshells, and have the potential to be

used as low cost parent materials. The nature of organic precursors used as feedstock, in addition to the production conditions, has important impact on char formation and type of porosity. The textural properties of raw material can generally be tracked in the final product, being influential in the particle shapes, density and type of porous structure (Sharifan 2013) as observed in Figure 2.3 which shows the scanning electron microscopy (SEM) images of AC derived from different raw materials.

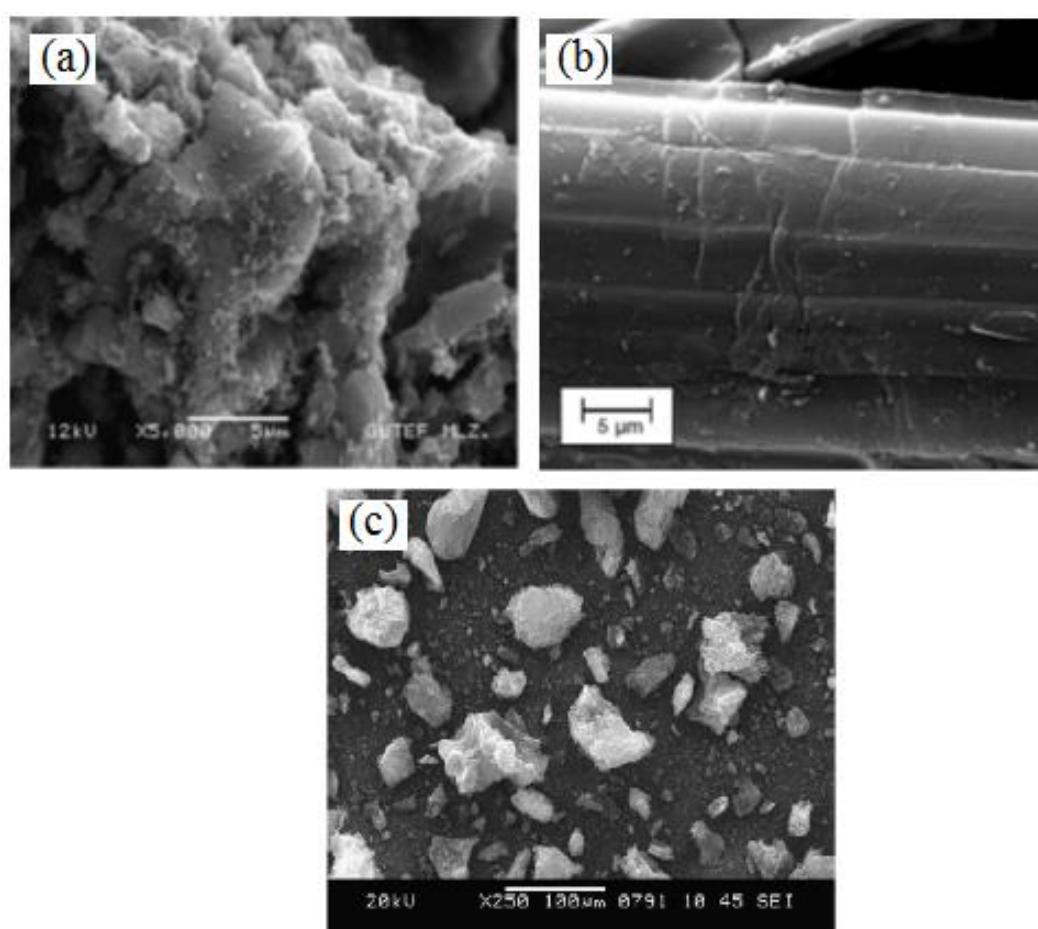


Figure 2.3 SEM images of activated carbons from various raw materials (a) Waste tea; chemical activation with H_3PO_4 at 350°C for 72 h (Yagmur *et al.*, 2008), (b) Flax fiber; steam activation at 800°C (Williams and Reed, 2006), (c) Soy bean oil cake; chemical activation with K_2CO_3 at 800°C (Tay *et al.*, 2009): Scale 5 μm for (a) and (b), and 100 μm for (c).

Raw materials are classified as softwood, hardwood, lignin, or shells and these have slightly varied % carbon range, % volatile and % ash content as shown in Table 2.4. Coal precursors have higher carbon content than other materials.

Table 2.4 Characteristics of various conventional raw materials used for making AC (Manocha, 2003).

Raw materials	Carbon (%)	Volatile (%)	Ash (%)	Texture of AC
Softwood	40-45	55-60	0.3-1.1	Soft, large pore volume
Hardwood	40-42	55-60	0.3-1.2	Soft, large pore volume
Lignin	35-40	58-60	-	Soft, large pore volume Hard, large multi pore volume
Nut shells	40-45	55-60	0.5-0.6	
Hard coal	85-95	5-10	2.15	Hard, large pore volume

2.3.2 Temperature

The final activation temperature affects the characteristic of the produced activated carbon such as the yield and surface area. Temperatures as high as 800°C have been employed for activation of ACs by steam or CO₂ (San-Miguel *et al.*, 2003). Researchers have been recently working on optimizing the final activation temperature to economize the cost of production and time. Literature shows that a wide range of temperatures have been utilized. These include low temperature of about 200°C (Haimour *et al.*, 2005), moderate temperature 400-500°C (Srinivasakannan *et al.*, 2003) and very high temperatures of 1100°C (San-Miguel *et al.*, 2003). Guo *et al.* (2003) observed that increasing activation temperature reduces the yield of the AC due to the increasing amount of volatiles which are released between 500°C and 900°C.

Haimour *et al.* (2005) suggested that the percentage of volatile matter decreased with an increase in carbonization temperature from 200 to 800°C. Haimour *et al.* (2005) stated that it was unsuitable to prepare AC at carbonization temperature above 800°C due to minimal release of volatile matter beyond this temperature. The effect of carbonization temperature on quality of ACs was followed by measuring the surface area (Haimour and Emeish, 2006). It was observed that the surface area increased with increase in carbonization temperature with optimal temperature of 700°C. The increase in surface area was ascribed to the release of volatile matter leading to the development of pore sites (Haimour and Emeish, 2006).

2.3.3 Activation time

Besides activation temperature, the activation time also affects the carbonization process and properties of activated carbon. The activation times used ranged from 1 to 3 hours for palm shell and coconut shell (Srinivasakannan and Zailani, 2003). As the time increased, the percentage yield decreased gradually while the BET surface area increased. This was attributed to the volatilization of organic materials from raw material which resulted in formation of activated carbon. The extent of decrease in the product yield was attributed to an excessive activation time (Srinivasakannan and Zailani, 2003).

2.4 Classification of activated carbons

The classification of activated carbons is difficult due to their complex products and is based on their preparation methods, physical properties, and surface characteristics. The general accepted classification of activated carbons is however based on particle size which divides them into 3 groups namely, powdered

activated carbon (PAC), granular activated carbon (GAC), and activated carbon fibres (ACF) (Babel and Kurniawan, 2003).

2.4.1. Powdered activated carbon

Powdered activated carbon (PAC) has a typical particle size of less than 0.1 mm and the common particle size ranges from 0.015 to 0.025 mm. Typical applications of PAC include industrial and municipal wastewater treatments, sugar decolorization, in food industry, pharmaceutical, and mercury and dioxin removal from a flue gas stream (Cook *et al.*, 2001; Zhang *et al.*, 2006; Ormad *et al.*, 2008; Satyawali and Balakrishnan, 2009).

2.4.2. Granular activated carbon

Granular activated carbon (GAC) has a mean particle size ranging from 0.6 to 4 mm. It is commonly used in continuous processes of both liquid and gas phase applications. Advantages of GAC over PAC include a lower pressure drop, regeneration, re-use, proper micropore size distribution, high apparent density, high hardness, and a low abrasion index. These properties have made GAC more suitable for various applications as compared to PAC. An example of an industry in which PAC is not used is the mining industry. This is because PAC can be sieved through the carbon in pulp screen together with the waste, which leads to a loss of gold. PAC's small particle size also makes it to be less resistant to attrition and this poses a drawback for employing it in the circuits (Hai *et al.*, 2011). Figure 2.4 shows a typical granular form of activated carbon.



Figure 2.4: Granular form activated carbon (Abdulqadir, 2014)

2.4.3. Activated carbon fibers

Activated carbon fibers (ACFs) are carbonized carbons which have been subsequently heat treated in an oxidizing atmosphere. ACF was first developed in 1970 using the viscose rayon precursor which consisted mainly of cellulose. Recently thermoset polymer materials like saran and phenolic resins have been used as precursors to produce ACF (Menendez-Diaz and Martin-Gullon, 2006). It has been found that a good ACF precursor must be non-graphitic and non-graphitizable carbon fibre which is isotropic in nature. Since the end of 1980s, an interest has been centered on the production of ACFs from various inexpensive precursors (Nahil and Williams, 2011).

2.5 Main applications of activated carbon

The unique adsorptive properties of activated carbon have made it an important commodity in many industries for purification and separation purposes. Removal of colour, odour, taste and undesirable organic and inorganic impurities from water has been one of the most common liquid phase applications for activated carbons.

Moreover, ACs have been applied in purification of air, as well as other gases such as hydrogen, carbon dioxide, natural and landfill gas. Solvent recovery, food processing, gold and silver recovery and application as a catalyst or catalyst support are other applications of ACs (Bansal *et al.*, 2005). In general, the primary applications of activated carbon can be categorized into two groups; gas and liquid phase adsorption, of which some examples are presented in Table 2.5.

Table 2.5 Application of activated carbons (Bansal *et al.*, 2005).

Liquid Phase	Municipal water treatment: Taste and odour removal - micropollutant removal (e.g. pesticides, THMs).
	Domestic water treatment: Jug filters, in-line filters, cartridge filters
	Process water treatment: Hydrocarbon removal from condensate, trace organics removal
	Waste water and ground water treatment: Trace organics removal.
	Food industry: Fusel oil removal from beverages, removal of undesirable flavours and improve colour, decaffeination of coffee beans.
	Sugar, oil and fat refining: To improve colour, higher rates of crystallization (sugar industry).
	Medicine: removal of bacterial toxins, treating gastritis and poisoning caused by mushrooms, food, phenols and phosphorus.
Gas Phase	Gold and silver recovery.
	Gas purification: Hydrogen, natural gas, carbon dioxide, landfill gas.
	Air treatment: Decolourisation, vapour removal (e.g. vent filters, anesthetics, compressed air) – solvent recovery - ductless fume cupboards, war gas protection filters, industrial and military respirators,
	incinerator flue gas, cooker hoods, deep fryers

2.6 Structure of activated carbon

2.6.1 Physical structure of activated carbon

Carbonized materials have two different well-defined types: non-graphitizing carbon and graphitizing carbon. These differences in structure were found to be obvious from the earliest stages of carbonization (Zhao *et al.*, 2009). Generally, the substances that have a high ratio of oxygen or a low ratio of hydrogen content are called non-graphitized carbon. The non-graphitized carbons demonstrate a strong order of cross linking of crystallites during heating at low temperature, forming a porous carbon. This leads to a random orientation of the crystallites in a rigid, finely porous mass. The neutron diffraction studies showed that non-graphitizing carbons consist entirely of sp^2 hybridized atoms (Zhao *et al.*, 2009).

The structures of non-graphitizing carbon were related to that of fullerenes (Harris *et al.*, 2008). Such structures could explain the micro-porosity of the carbon and many of its other properties (Abdulqadir, 2014). AC is much closer to graphite in properties and structure. Graphite is composed of layers of fused hexagons held by weak Van der Waals forces. These layers are held by carbon–carbon bonds (Harris *et al.*, 2008). Regarding the structures, interlayer spacing in graphite is 0.335 nm. AC is a muddled form of graphite, as a result of the presence of impurities and the activation process. The interlayer space in AC ranges between 0.34 nm and 0.35 nm. Activation temperatures and carbonization produced more enhanced structure.

2.6.2 Porous structure

The high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume, and pore size distribution. The

characteristics largely depend on the nature of the raw material and activation process route. The pore dimensions, and porous structures are categorized by an IUPAC7 approved classification to be microporous with pore width <2 nm, mesoporous with pore width of 2-50 nm and macroporous with pore width of >50 nm (Figure 2.5). Generally the microporous structure of an adsorbent is characterized by adsorption of gases and vapors and, to a small extent, by small angle X-ray technique (Yang and Lua, 2006; Rosas *et al.*, 2009; Zuo *et al.*, 2009; Liou, 2010; Castro-Muniz *et al.*, 2011) enhance mesopores attaining a volume of 0.2 to 0.65 cm³/g and surface area of 200 m²/g. Capillary condensation and adsorption-desorption hysteresis are the characteristic features of mesopores (Lei *et al.*, 2006; Awornetal, 2008; Hao *et al.*, 2011).

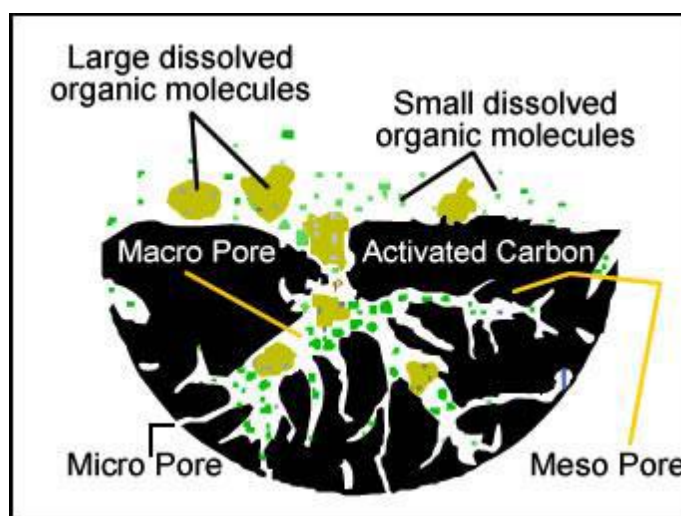


Figure 2.5: Micropore, mesopore and macropore regions of activated carbon (Abdulqadir, 2014)

Beside their contribution to the adsorption of adsorbate, mesopores act as conduits which lead the adsorbate molecule to the micropore network. The typical pore size distribution of activated carbon can be observed in Figure 2.5. Generally, mesopores are characterized by adsorption-desorption isotherms of gases, by

mercury porosimetry, and by electron microscopy (Zhu *et al.*, 2007; Kennedy *et al.*, 2007; Liou, 2010).

2.6.3 Chemical structure

The adsorption capacity of AC is dependent on its porous structure as well as the chemically bonded heteroatom (mainly oxygen and hydrogen) (Bansal *et al.*, 2005). Much of the literature show that the heteroatoms are bonded to carbon atoms on the edges and corners of the aromatic sheets or to the carbon atoms at defect positions to form carbon-oxygen, carbon-hydrogen, carbon-sulfur, carbon-nitrogen, and carbon-halogen surface compounds, known as surface groups or surface complexes (Valix *et al.*, 2006; Castro-Muniz *et al.*, 2011). A hypothetical structure of AC is given in Figure 2.6. The variation in the arrangement of electron clouds in the carbon skeleton results in the creation of unpaired electrons and incompletely saturated valences which influences the adsorption properties of ACs, mainly for polar compounds. A considerable effort has been directed to identify the role of surface chemistry of carbons on the adsorption of metals from aqueous solutions (Namasivayam *et al.*, 2007; Duman and Ayranci, 2010; Shen *et al.*, 2010; Mamcilovic *et al.*, 2011; Zhang *et al.*, 2011).

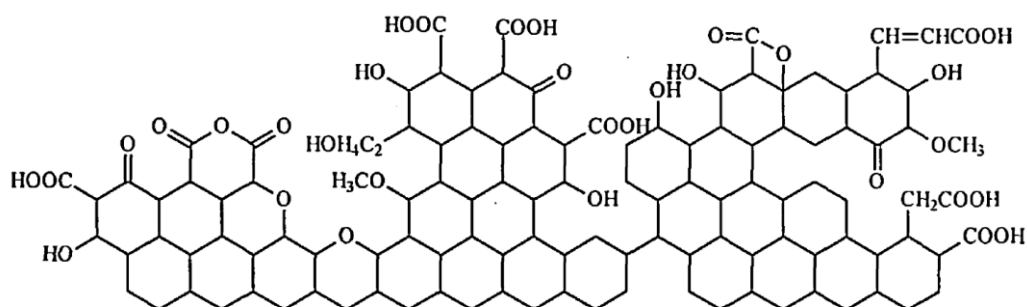


Figure 2.6 Model structure showing a fragment of oxidised carbon (Jia, 2000).

AC has the ability to remove even small quantities of metal ions from wastewater because of the formation of compounds surface between metal ions and the acidic surface functional groups of activated carbon. The effectiveness of AC in pollutant removal is linked to several factors including concentration of the solution, solution pH, ionic strength, formation method, chemical nature and its physical properties (Fong *et al*, 2012). However, the adsorption rate of the AC can be enhanced if it is modified or made to interact with chelating agents as was discussed in section 2.4. Simple metal ions such as mercury ions have been observed to be poorly adsorbed due to their good solvation in aqueous solution and the hydrophobic nature of ACs. The adsorption rate of metal ions can be enhanced by pre-treatment of activated carbon with some appropriate chemical reactions such as precipitation, oxidation-reduction reaction, acid-base reaction or neutralization, complex formation, hydrolysis and catalytic reactions. In this way, AC can combine with simple metal ions to produce precipitation, complexes or chelates and this in turn can enhance adsorption of metal cations significantly (Zhang *et al.*, 2011). Oxygen is by far the most important heteroatom that influences the surface behaviour, wettability, polarity, acidity and catalytic properties of carbon.

Hence, in this study the activated carbons were modified with HNO_3 and H_3PO_4 in order to increase the oxygen content on the activated carbons.

2.7 Characterization and properties of activated carbon

Physical properties of AC include ash content, moisture content, and volatile matter. The specific surface area and surface chemistry (wettability, polarity, acidity and catalytic) are examples of chemical properties. These properties can affect the use of GAC and render them either suitable or unsuitable for adsorption

of metal ions. Various techniques such as Brunauer-Emmet-Teller (BET), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), elemental analysis (EL) and X-ray diffraction spectroscopy can be used to evaluate the surface chemistry, morphology and texture of AC.

2.7.1 Surface area

Typically, surface area for commercial activated carbons range from 600-1200 m²/g (Guo and Lua, 2003). Larger specific surface areas have been related to better adsorption performance (Guo and Lua, 2003). Surface area is a measure of pore volume, pore size and channels present in an adsorbent. The pore volume limits the size of the molecules that can diffuse and adsorb whilst the surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size (Lei *et al.*, 2006; Hao *et al.*, 2011). The specific surface area (m²/g) of porous carbon is usually determined from gas adsorption measurement using the BET theory (Hu and Srinivasan, 1999). The most commonly employed method to characterize these structural aspects of the porosity is based on the interpretation of adsorption isotherm (e.g., N₂ at 77K).

2.7.2 Moisture content

Knowing the moisture content of activated carbons prior to purchase is important because AC is sold by weight and untrustworthy dealers can take advantage of the buyer by selling them a lesser quantity due to the weight discrepancy caused by the moisture content. Some ACs when stored under humid conditions will absorb considerable moisture over a period of a month unless packaged in airtight containers. They may adsorb as much as 25 to 30% moisture and still appear dry.

Abiko *et al.* (2010) performed a study on the reduction of adsorption capacity of coconut shell activated carbon for organic vapours due to moisture contents. The relationship between moisture adsorption and the reduction of the break through time of activated carbon specimens were carried out and further measurements of the effect of moisture content on the adsorption of 13 kinds of organic vapour was also investigated. The results showed that the presence of moisture in ACs generally decreased the adsorption capacity for organic vapours. Sivakumar *et al.* (2012) also performed a study on the physico-chemical and adsorption studies of activated carbon from agricultural wastes.

Low moisture content indicated that the carbon samples had poor affinity for water (Sivakumar *et al.* 2012). It was also observed that though moisture content of the carbon doesn't affect the adsorptive capacity, it dilutes the carbon which demands the use of additional weight of carbon during treatment processes. Therefore, an additional weight of moist carbon is needed to provide the required dry weight. In a study done by Silgado *et al.* (2014) on adsorption of chromium(VI) by ACs produced from oil palm endocarp, the ACs used showed high significant moisture values which required appropriate packaging, transportation and storage conditions for moisture control.

It was concluded that moisture content must be carefully considered in order to obtain an acceptable product that can be used for environmental applications as pellets or powder carbons. In literature although researchers have determined moisture content in the purpose of using activated carbon for the adsorption of gold much is not said about its effects on the adsorption process.

2.7.2 Ash content

The ash content of a carbon is defined as the residue of inorganic material that remains when the carbonaceous materials is burned off. This residue is measured as ash content, generally in the range between 2 and 10% (Yang, 2003). The total amount of inorganic constituents usually varies from one grade of carbon to another depending on the source materials and activating agents added during manufacture. Ash content can lead to increase in hydrophilicity and catalytic effects, causing restructuring during the process of regeneration for the used activated carbon (Yang, 2003). Ash in ACs is an impurity and an undesirable product. A good AC must have low ash content. A small increase in ash content causes a decrease in adsorptive properties of activated carbon. Likewise, the quality of ACs used in the present study was evaluated by measuring the ash content.

2.7.3 Volatile matter

Volatile matter is the material that is driven off when AC is heated to 950°C in the absence of air under specified conditions. It is measured practically by determining the loss of a mixture of gases, low-boiling-point organic compounds that condense into oils upon cooling. Volatile matter in AC may be used as a relative measure of the extent of carbonization and the extent of loading of volatile material that has been used on an adsorption application. The volatile content of quality AC can go up to 40% and it is perceived that the higher the volatile content, the more the AC will be resistant to attrition. Although the volatile matter can go as high as 40%, it should not exceed 40% as this was found to lower the adsorption capacity of ACs (Yang, 2003).

2.7.4 Attrition

Attrition is the wearing off and weakening of carbon surface strength as a result of continuous pressure. In the mining industry application attrition is mainly caused by carbon to carbon interaction, exposure to high temperatures and collisions during the inter-stage pumping of the carbon-in-the-pulp-circuit. Attrition is one of the major contributors to fine carbon generation. Activated carbon with high attrition rate is considered to be of less quality in the mining industry. Fine carbon generation results in high consumption of carbon, less life span of carbon in the carbon in pulp circuit and precious metal loss due to fine carbon escaping through the screens together with the residue in the adsorption circuit (Elnathan, 2007).

Typical pre-abrasion test results for a good quality activated carbon are around 95–99%. However, AC with values lower than 95% are considered of lower quality for use in most carbon in pulp processes. Abrasion percentage values between 89% and 92% are still considered to be reasonably satisfactory while an abrasive percentage of 75% or less represents a softer/poorer quality activated carbon (Marsh, 2001). Therefore, for carbon to have a good attrition resistance it must have less than 2% carbon losses in 24 h.

2.8 Adsorption

2.8.1 Physisorption and chemisorption

The term adsorption, first introduced by Kayser in 1881, is internationally defined as the enrichment of one or more of the components in the region between two bulk phases or interfacial layer. Adsorbent is the term used for the solid onto which adsorption takes place and adsorbate is the compound retained by adsorbent (Gregg and Sing, 1982). Depending on the forces involved, adsorption of analytes on the

porous structure may be due to either physical or chemical bonding. The physical adsorption or physisorption takes place due to the short range repulsive forces, called Van der Waals dispersion forces or intermolecular forces. These forces are generated between the adsorbent-adsorbate atoms by rapid fluctuation of electron density within each atom. The fluctuations induce an electrical moment in a neighbour atom thus, resulting in attraction between the two atoms (Gregg and Sing, 1982). Physisorption is not site-specific, implying that it can take place on an entire surface of solid and with any molecule.

Once the surface of the solid is covered by the first layer of adsorbate molecules, another layer can form on top, referred to as multilayer adsorption. Adsorption of most gases on porous solids is of this type. Unlike physisorption, the chemical adsorption or chemisorption is the adsorption in which chemical bonds are involved, mainly by exchange or sharing covalent electrons between the active groups on adsorbent and adsorbate surfaces. Chemisorption takes place in monolayer only, is site-specific and involves stronger forces than Van der Waals forces due to the formation of chemical bonds (Bansal and Goyal, 2005). Factors affecting adsorption differ according to the material being adsorbed, these include: mass of adsorbent, time, initial concentration of adsorbate, temperature, pressure, and ionic strength. In cases of adsorption of precious metals like gold, the primary requisites are high adsorption capacity, high adsorption rate, low moisture content, low ash content, low volatile matter and good resistance to attrition. The adsorption step is critically important as the Au that is not adsorbed during the adsorption stages is a loss to the mines. Table 2.6 illustrates the differences between the physical and chemical adsorption methods. The AC that undergoes physical adsorption is easier to regenerate compared to the AC that has undergone chemical

adsorption. This is because the AC that has undergone chemical adsorption has its surface chemistry been changed due to electron transfer leading to bond formation between adsorbate and adsorbent. Reversing the formed bonds after leaching the adsorbate is difficult to achieve.

Table 2.6 Differences between physical and chemical adsorption (Bansal and Goyal, 2005)

Physical Adsorption	Chemical Adsorption
Low heat of adsorption (< 2 or 3 times latent heat of evaporation)	High heat of adsorption (> 2 or 3 times latent heat)
Non specific	Highly specific
Mono or multi-layer	Monolayer
No dissociation of adsorbed species	May involve dissociation
No electron transfer although polarization of adsorbate may occur	Electron transfer leading to bond formation between adsorbate and surface

2.8.3 Mechanism of Au adsorption

In the mining industry gold first undergoes cyanidation process before it is adsorbed onto the activated carbon. According to Finkelstein (1972), most of the gold dissolves according to the following reaction:

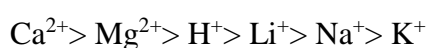


The cyanidation of gold occurs through the above-mentioned reaction, and this results in aurocyanide complex being formed, which is important for the following adsorption study. The mechanism of adsorption of aurocyanide by ACs has been a subject of disagreement and controversy, and despite the commercial importance of the process no consensus has been reached as yet. Mpinga (2012) recently found

this still to be the case and that no complete agreement of the adsorption mechanism exists. The most widely accepted theories are:

- adsorption involving ion pairs, $Mn^+[Au(CN)_2]^-$
- adsorption of unpaired $[Au(CN)_2]^-$ ions onto activated carbons
- decomposition of other species such as AuCN, Au or a partially reduced state.

According to Adams (1991), the above-mentioned mechanisms have all been shown and can operate under various conditions of ionic strength and pH value. Davidson *et al.* (1979) showed that the extraction of aurocyanide by carbon was enhanced by the cation present in solution. The order of enhancement for group IA and IIA cations is given by the following series:



In addition to the cationic effect, McDougall *et al.* (1991) witnessed that the ionic strength of the additive also influenced the equilibrium aurocyanide adsorption. Small increases in ionic strength greatly enhanced the adsorption, although this effect was found to levelled off after ionic strengths reached a concentration greater than ~0,20 M. One can conclude that the effect of cation on the adsorption of aurocyanide is probably due to the extraction of neutral ion-pairs by carbon. The enhanced adsorption capacity observed due to the increase in ionic strength shifted the equilibrium to the right-hand side as expected by Le Chatelier's principle. The functional groups developed during the activation process were responsible for the adsorption of the Au complex onto the carbon surface (Tsuchida, 1986) but are not well understood. It was speculated that the form of the adsorbate changes when the surface is impregnated by gold.

2.8.5 Studies on the adsorption of gold by activated carbon

Activated carbons derived from hard shells of Iranian apricot stones were investigated for gold recovery from electro-plating wastewater (Soleimani, 2007). The effect of parameters such as adsorbent dose, particle size of adsorbent, pH, and agitation speed of mixing on the gold recovery were investigated. The results showed that under the optimum operating conditions more than 98% of gold ions were adsorbed onto activated carbon after just 3 h. In addition, the adsorbed gold could be eluted from the adsorbent by an improved stripping method. Poinern *et al.* (2011) investigated the adsorption of aurocyanide, on granular activated carbons derived from *Macadamia* nut-shells. The processing of the *Macadamia* nut-shells commenced with the carbonization of the shells under nitrogen. This was followed by the physical activation of the shells under carbon dioxide at different temperatures to investigate the effect of the activation temperature on pore formation. The pore structure and gold loading capacity of the synthesized ACs were investigated. The porous nature and surface structure of the *Macadamia* shell based activated carbon were examined by SEM at various stages of manufacture. In conjunction with gold loading studies, elemental mapping of the AC surface to determine the gold adsorption sites was also investigated. The study revealed that activated *Macadamia* shell based carbons have a strong affinity for the Au(I) complex and a potential to adsorb significant levels of gold. Benjamin *et al.* (2014) derived activated carbons from palm kernel shell employing leachates from cocoa husk using crude potash and pure potash K_2CO_3 as activating agents at 800°C activation temperature. The statistical tool of t-test (fresh carbon activity, hardness, ash content and apparent density at 95% confidence interval) was used to determine the statistical difference. No significant difference existed in the quality indices in

relation to gold mine operations of the produced AC using pure K_2CO_3 and crude potash as activating agents. Increasing activation/ carbonization temperature was found to enhance the fresh carbon activity and apparent density for both AC.

Depci *et al.* (2014) did a study for the applicability and suitability of the obtained low-cost activated and magnetic ACs for gold adsorption and elution process. The activated carbons were prepared from Turkish lignite (LAC) by impregnating lignite with distilled water and KOH mixture in 1:4 ratios. A magnetic activated carbon (MgAC) was prepared by 0.5 g of the modified LAC in 20 mL of an aqueous solution containing 4 g of $Fe(NO_3)_3 \cdot 9H_2O$. The effects of various experiments such as initial gold concentration, pH and adsorbent dosage were investigated in a batch adsorption technique. The prepared ACs were compared with the commercial ACs (CrAC). The percentage of gold adsorption onto activated carbon LAC and MgAC showed the same trend as CrAC as they absorbed more than 80% of gold in 15 min and nearly 100% in the next 45 min. On the other hand the granular carbon adsorbed only 30% in 15 min and 65% in 45 min due to the particle size effect.

2.9 Summary and significance of literature review

Activated carbons can be produced from different waste biomass (e.g. rice husk, olive waste and nut shells) and have been investigated for their adsorptive properties by numerous researchers, some of which have been summarized in this chapter. The objective of these studies was mainly to provide low cost adsorbents by using abundant raw natural material for the production of a valuable filter and adsorbent for gold recovery. The statistics from the Food and Agricultural Organisation (FAO) showed that *Macadamia* shells are annually produced in large amounts as *Macadamia* has become one of the most important crops in South

Africa (Mogale, 2012). It was established that the shells were generally discarded and treated as low-value products. However, being a highly carbonaceous material, they were found to be a suitable raw material for the production of activated carbons. The literature review emphasised on the importance of the starting material, activation temperature, activation time which strongly affect the unique properties of activated carbon, *i.e.* its high surface area, porosity and adsorption capacity.

In addition, the work is different to the study done by Poinern *et al.* (2011) firstly because CO₂ was used as activating agent while ours was produced by steam activation. Secondly, ACs in the present study further undergone secondary treatment with HNO₃ or H₃PO₄ which have never been used before in other studies in literature for the selective adsorption of gold. Thus it was imperative to investigate how locally produced *Macadamia* AC would perform in gold recovery in the mining recovery waste solutions in comparison to commercial coconut activated carbon. In addition, chemical oxidation of ACs not only produce oxygenated functional groups that can bind metal ions but it can also lead to damage of the carbon structure. Therefore, chemical environments that will lead to optimum results (no disintegration but higher loading capacities) ought to be investigated. The next chapter will introduce the aims and objectives set out to be achieved throughout the course of this dissertation.

CHAPTER 3: RESEARCH AIM AND OBJECTIVES

3.1 Aim

The aim of this research was to conduct a study in which HNO_3 and H_3PO_4 modified *Macadamia* activated carbons were compared to commercial coconut based activated carbons for the recovery of gold.

3.2 Objectives

- The specific objectives of this study were to:
 1. Modify the commercially prepared *Macadamia* activated carbons with different concentrations of nitric acid and phosphoric acid.
 2. Study attrition, ash content, volatile matter, and moisture content of all the activated carbons.
 3. Characterize the modified *Macadamia* and coconut activated carbons using elemental analysis; Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM) and X-ray diffraction (XRD). However, due to the unavailability of some instruments, only few samples were selected to be characterized.
 4. Study and compare the effect of parameters on adsorption of gold such as initial concentration, time, agitation speed, interfering species and dose of the adsorbent on the rate of adsorption for gold
 5. Study the re-usability and application on real samples of the modified activated carbon

3.4 Hypothesis

Surface modifications of *Macadamia* activated carbon with nitric acid and phosphoric acid will produce a carbon adsorbent with qualities superior to its unmodified version.

CHAPTER 4: MATERIALS AND METHODS

The focus in this chapter is on listing the chemicals and materials used in the study as well as elaborating on methods employed for preparation of the modified *Macadamia* activated carbons. Furthermore, the preparation of buffers, real samples and sampling techniques are detailed.

4.1. Materials and reagents

Potassium aurocyanide, calcium chloride, caesium chloride, sodium hydroxide, sodium cyanide, lanthanum chloride, nitric acid and phosphoric acid were purchased from Labchem (Johannesburg, South Africa). All chemicals used were of reagent grade. *Macadamia* nutshell activated carbons were sourced from Filtatech Activated Carbon Innovations (Boksburg, South Africa) while coconut shell based activated carbon were obtained from Jacobs Company (Johannesburg, South Africa).

4.2. Chemical characterization of activated carbons

Chemical characterization of activated carbon was determined by various instrumentation techniques such as elemental analysis (EL), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), Thermogravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) instrument.

4.2.1 FTIR

A PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer (Waltham, MA, USA) with wavenumber range of 4000 to 650 cm^{-1} was used to record the absorption

spectra of activated carbon samples. The machine is equipped with attenuated total reflectance and 26 scans were averaged.

4.2.2 SEM

Surface morphological information of coconut coir and *Macadamia* derived activated carbon was obtained using a scanning electron microscope (SEM) JOEL Model JSM 6700F (Tokyo, Japan).

4.2.3. BET

A Brunauer-Emmett-Teller (BET) instrument (MicromeriticsTristar) was used for the surface area determinations. The protocol followed for analysis is given below: At least about 200 mg of samples were degassed in N₂ at 150°C overnight prior to analysis using a Micromeritics Flow Prep 060, sample degas system. The surface areas and pore size distributions were then obtained at -196°C. The pore size distribution with specific surface areas of the sample, were determined via N₂ adsorption/desorption according to the BET method using a MicromeriticsTristar, surface area and porosity analyser. In order to confirm the accuracy of the results, the analysis was repeated at least twice for all samples and the results given are the averages.

4.2.4. Thermal gravimetric analysis

The thermogravimetric analysis (TGA) and differential thermo-gravimetric analysis (DTG) were performed to analyse the thermal degradation characteristics of the activated carbon samples. The weight loss was calculated as a function of temperature, using PYRIS-1 TGA, Perkin Elmer instrument (Waltham, MA, USA). Approximately 5 mg activated carbon were placed in a platinum crucible on the

pan of a microbalance and then heated between 25°C and 900°C at a heating rate of 5°C/min under nitrogen flow.

4.2.5 CHNS analysis

Elemental analysis of activated carbons was collected on a Thermo Flash 2000 series CHNS/O Organic Elemental Analyser. The carbon, nitrogen and hydrogen contents were directly determined while the oxygen content was calculated by difference assuming only these elements were present.

4.2.6 X-ray diffraction spectroscopy

The extent of graphitization in prepared ACs was determined by an X-ray diffractometer (Shimadzu X-RD-7000) (D8 ADVANCE, Bruker, USA). Scans were run with a step size of 0.02°/s of 2Θ , typically in the angle range between 10° and 80°.

4.2.7 Atomic absorption spectrometer

The concentration of gold and other base metals was measured using an atomic absorption spectrophotometer AA-7000 from Shimadzu (Kyoto, Japan).

4.3 Physical characterization of activated carbons.

Physical characterization of activated carbons included the determination of ash content, moisture content, volatile matter, and attrition. The analyses were all done in duplicate to confirm the values and the reported values are the means.

4.3.1 Determination of moisture content

Activated carbon (50 g) was weighed and placed in an oven overnight at 105–110°C. It was then cooled in a desiccator and weighed to a constant mass.

4.3.2 Determination of ash content

One gram of the activated carbon was weighed into a crucible and placed in an electric furnace at 650°C for 1 hour. The sample was removed from the furnace and placed in a desiccator for cooling. The sample was weighed on a balance. Ashing of the activated carbon was carried out for 3 to 8 h depending on the type of activated carbon and its particle size; ashing was completed only when the constant mass had been achieved.

4.3.3 Determination of volatile matter

One gram of the activated carbon was weighed into a crucible and placed in an electric furnace set at 900°C for seven minutes. The activated carbon was then transferred into a desiccator for cooling and weighed. The moisture of the activated carbons was pre-determined in order to calculate the volatile matter.

The volatile matter content is given by:

$$v = \frac{100[100(B-F) - M(B-G)]}{(B-G)(100-M)} \dots\dots\dots (4.1)$$

where,

B= mass in g of lid, crucible and sample before heating

F= mass in g of lid, crucible and sample after heating

G= mass in g of the empty crucible with lid.

M= moisture as a percentage of mass

4.3.4 Determination of attrition

The hardness was determined by the wet attrition method of Toles *et al.* (2000).

One gram (1.0 g) of the activated carbon was placed in 100 mL of 0.1 M acetate buffer in a 150 mL beaker. The solution was stirred at 500 rpm for 2 h at ambient

temperature. The sample mixtures were then poured on a 0.30 mm screen and washed sequentially with 250 mL of distilled water. The retained samples on the screen were transferred onto an aluminum pan and dried in the oven at 110°C for 2 h. The samples were finally cooled in a desiccator. The percent attrition or hardness is calculated using the equation:

$$\text{Attrition (\%)} = \frac{A-B}{A} \times 100 \dots\dots\dots (4.2)$$

where, A= initial mass; B= final mass

4.4 Preparations of stock and working solutions

4.4.1 Gold solution

A stock solution (100 mg/L) of gold was prepared by dissolving dried potassium auro cyanide, $K_2Au(CN)_2$ (analytical reagent grade) in Milli-Q water. Working solutions were prepared daily from the stock solution through serial dilutions. The stock solution was stored at room temperature when not in use. The pH was adjusted using dilute HCl or NaOH solutions.

4.4.2 Lanthanum chloride solution

A stock solution was prepared by weighing 10.6 g of lanthanum chloride into a 1000 mL made to the mark using distilled water. Working solutions were prepared daily from the stock solution through serial dilutions. The stock solution was stored at room temperature when not in use. The purpose of lanthanum chloride ($LaCl_3$) was to correct the interferences caused by the AA Spectrophotometer. $LaCl_3$ was added so it can complex with Ca to form stable compounds.

4.4.3 Sodium cyanide solution

A stock solution was prepared by weighing 18.84 g of sodium cyanide into a 1000 mL and made to the mark using distilled water. Serial dilutions of stock solution afforded the working solutions. The stock solution was stored at room temperature when not in use.

4.4.4 Calcium chloride solution

A stock solution was prepared by weighing 27.69 g of calcium chloride into a 1000 mL and made to the mark using distilled water. Working solutions were prepared daily from the stock solution through serial dilutions. The stock solution was stored at room temperature when not in use. The purpose of calcium chloride was to simulate the plant condition.

4.5 Preparations of buffer solution

Preparation of 0.1 M borate buffer was carried as follows; 3.09 g of boric acid (H_3BO_3) with molecular mass of 61.83 g/mol was weighed together with 3.73 g of potassium chloride (KCl) with molecular mass 74.56 g/mol and transferred into a 1000 mL volumetric flask. The pH of the solution was then adjusted to pH 10 with sodium hydroxide (NaOH) and filled to the mark using distilled water. Buffer solution was used to wet the carbon prior to use to displace the air entrapped in the carbon.

4.6 Preparation of *Macadamia* activated carbons

4.6.1 Nitric acid modification

In the impregnation process, 10 g of AC was impregnated with 30 mL of HNO_3 solution w/v (20%). The conical flask was enclosed with parafilm. Few holes were

punched onto the parafilm in order to let the vapors evaporate. The mixture was put onto a Protech 721 orbital shaker for 3 days to dissolve the solution. After drying, the product was transferred to a Pyrex petridish. The petridish was weighed before use. The chewy liquid product formed was further dried in the oven at 120°C for 24 h. Thereafter, the impregnated AC was weighed and put into the muffle furnace. After the AC was subjected to heat in the muffle furnace, the product was neutralized with the buffer solution and washed with distilled water thoroughly. The modified product was labeled MACN_{20%}. The same procedure was followed but using w/v (40 and 55%) of HNO₃ and the resulting products were labeled MACN_{40%} and MACN_{55%}.

4.6.2 Phosphoric acid modification

The same procedure as stated in sub-section (4.6.1) was followed for the modification of *Macadamia* activated carbon with phosphoric acid. The studied concentrations were (20, 40 and 60%) w/v of H₃PO₄. The resultant modified carbons were labeled as MACP_{20%}, MACP_{40%} and MACP_{60%}.

4.7 Adsorption Studies

4.7.1. Effect of dose of the adsorbent

Different amounts of activated carbon (1, 2, 3, and 4 g) were shaken for 60 min in a 2.5 L stoppered bottles containing 1 L aliquots of 5.7 mg/L gold cyanide at room temperature and at agitation rate of 150 rpm. The pH of the solution was adjusted to 10.0 using 0.1 M NaOH. This pH was chosen based on the two preliminary batch studies, where the activated carbon showed maximum adsorption around pH 10. After 60 min, exactly 5 mL of samples were then pipetted into a 25 mL volumetric

flask and to this 5 mL of lanthanum chloride was added. The residual gold concentration in the solution was analysed using AAS.

4.7.2 Effect of initial concentration on adsorption of gold cyanide

The effect of initial concentration on the extraction of gold cyanide by activated carbon was studied by shaking 1 g of material at room temperature for 60 min at agitation speed of 150 rpm. The initial pH of the solutions was adjusted to pH 10 using sodium hydroxide and the range of initial gold cyanide concentrations studied was 1, 2, 3, 4, 5 and 6 mg/L. The solution volume was again fixed to 1 L. Concentration of un-adsorbed gold cyanide was determined by AAS. All the experiments were conducted in duplicate and statistical methods were utilised to determine the mean values and standard deviations.

4.7.3. Effect of agitation speed

The effect of agitation speed on the adsorption of gold cyanide ion onto activated carbon was investigated by varying agitation speed 50-250 rpm for an hour. This was achieved by shaking 4 g of activated carbon in a 2.5 L stoppered bottle containing 1 L of 5.7 mg/L gold cyanide solutions. After 60 min, exactly 5 mL of samples were then pipetted in a 25 mL volumetric flask and to this 5 mL of lanthanum chloride was added. Two replicates were performed for each point. The residual gold concentration in the solution was analysed using AAS.

4.7.4 Effect of contact time

The effect of contact time on the extraction of gold cyanide by activated carbon was studied by shaking 4 g of activated carbon in 2.5 L stoppered bottles at room temperature with solution containing 5.7 mg/L of gold cyanide at agitation rate of 150 rpm in duplicate. The time intervals investigated were 60, 120, 180, 240 and

300 min. The solution volume used for such experiment was 1 L. After each shaking time, the amount of un-adsorbed gold was measured as described earlier.

4.7.5. Selectivity on adsorption of gold (effect of interfering species)

The selectivity of the prepared activated carbons for gold among its competitors was investigated in multi-element mixture analysis. The competitors examined were Ni, Cu, Fe and Pb. In multielement analysis all the four cations together with the gold were prepared in a single solution and the initial concentration of each analyte was 6 mg/L. 4 g of activated carbon was shaken in 2.5 L stoppered bottles at room temperature with solution containing 5.7 mg/L of gold cyanide and the selected cations at agitation rate of 150 rpm. The experiments were performed in a batch mode at optimum conditions and the remaining concentrations of each anion were measured using AAS.

4.7.6. Reusability of HNO₃ activated carbon

Regeneration of activated carbon was investigated by contacting 4 g of AC with gold solution having an initial concentration of 6 mg/L for 6 h. Optimum conditions obtained from other previous experiments were used for other variables. After extraction and equilibration, the aqueous solution was filtered and the activated carbon particles were transferred to another sample vial. To strip out the adsorbed gold, activated carbon particles were boiled in HCl and agitated in a 1 L solution of NaOH (0.1 M) and NaCN for 30 min. This was followed by filtration and analysis of gold in the filtrate. The activated carbon particles were used for the next adsorption for five cycles without any conditioning.

4.7.7 Application to real samples

The applicability of the prepared activated carbons for the removal of gold species on real-world samples was carried out using a Barren sample solution from a gold plant. The pH of these samples was measured and subsequently adjusted to pH 10 where needed. The concentration of other base metals like Ni, Cu, Pb and Fe was

measured using an atomic absorption spectroscopy. For the experiment, 4 g of activated carbon in 1000 mL of the above-mentioned solutions were agitated for 6 h in 2.5 L. The experiments were performed in a batch mode at optimum conditions in duplicate and the remaining concentrations of each cation were measured using AAS.

4.7.8 Equations used to treat the data

Batch adsorption studies for each experiment were performed by agitating specified amounts of AC in plastic bottles containing a certain concentration and volume of the analyte molecule. After a specified experimental time had lapsed, some constants defining adsorption were calculated from such results. The adsorption binding constants calculated in this study were the adsorption capacity (Q , mg/g) as well as the percentage recovery (% R). Adsorption capacity of the activated carbon for a specific analyte was measured and calculated by the following equation (Birlik *et al.*, 2007):

$$Q = \frac{(C_0 - C_e)V}{W} \dots\dots\dots (4.4)$$

Where, C_0 and C_e is the initial and final concentrations respectively (mg/L), V is the volume of the solution used for the extraction (L) and W is the mass of the AC used for recovery (g) . Percent recovery (% R) was calculated using the following equation: where, all the terms have been previously described.

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots (4.5)$$

CHAPTER 5: RESULTS AND DISCUSSION

This chapter is divided into two subsections where Section 5.1, deals with H_3PO_4 modified activated carbons. The emphasis is on characterization, optimization of certain parameters and, application to real samples. The performance of the H_3PO_4 modified activated carbons was compared to the virgin carbons derived from *Macadamia* and coconut shells. Section 5.2, deals with HNO_3 modified activated carbons. Again characterization, optimization of certain parameters, application to real samples were looked into and these HNO_3 modified activated carbons, where again the same chemical attributes and performance were investigated in detail.

5.1 Modification of *Macadamia* activated carbons with phosphoric acid

A method adapted from Anisuzzaman *et al.* (2014) was used with modifications to prepare phosphoric acid modified activated carbons. The *Macadamia* activated carbons were modified with 3 different concentrations of phosphoric acid as stipulated in the experimental section. The surface properties of all prepared activated carbons were studied using various techniques and the results are discussed below. In addition, their gold cyanide ion adsorptive properties were also evaluated.

5.1.1 Instrumental characterization of phosphoric acid modified activated carbons

5.1.1.1 Elemental analysis

Elemental analysis was carried out to obtain the recent compositions of C, N, H and S atoms in the activated carbons (Table 5.1). After modification process with

H₃PO₄, it was observed that the carbon content of the modified activated carbons, (MACP_{20%}, MACP_{40%}, and MACP_{60%}) were lower than the unmodified activated carbon (MAC). This was assigned to the fact that during the activation step, the oxidation effect of H₃PO₄ involves an increase in O content and a decrease in C content (Phan *et al.*, 2006). The presence of oxygen leads to further decomposition of secondary organic matter at higher temperatures and changes morphology of the produced char, thus leaving a deep impact on the combustion characteristics (Lee *et al.*, 2014). In addition, the decrease in %C may possibly be due to increasing oxygen and phosphorus content from H₃PO₄ addition (Myglovets *et al.*, 2014) and progressive formation of phosphates/polyphosphates which are bound to carbon via C-O-P linkages within the temperature range of 500°C - 700°C. Similar results were observed in a study done by Mopoung *et al.* (2016).

Table 5.1 Elemental analysis of activated carbons

Type of carbon	CHNS analysis (%)				
	C	H	N	S	O*
CAC	89.05	<0.1	0.17	<0.1	10,78
MAC	83.27	1.53	0.5	<0.1	14,7
MACP _{20%}	79.66	1	<0.1	<0.1	19,34
MACP _{40%}	81.66	<0.1	0.26	<0.1	18,08
MACP _{60%}	78.22	<0.1	<0.1	<0.1	21,78

*Computed by difference

5.1.1.2 FTIR spectra of various activated carbons

Figure 5.1 shows the FTIR spectra of MAC, MACP_{20%}, MACP_{40%}, MACP_{60%} and CAC. It was observed that the spectra of the 5 types of adsorbents had a similar backbone typical of activated carbon biomass. Major changes were observed at approximately 3500, 1300 and 1000 cm⁻¹ wavenumbers. The band at about 3500 cm⁻¹ observed in MACP_{20%}, MAC and CAC was assigned to bonded and non-bonded hydroxyl groups.

The disappearance of this peak in MACP_{40%} and MACP_{60%} could be attributed to the elimination of hydroxyl in the presence of heat and H₃PO₄ to form alkenes, particularly in MACP_{40%} where CHNS analysis showed a decrease in % oxygen. Another notable change is the disappearing of the band at 1365 cm⁻¹ in MAC attributed to C-OH of the carboxylic group. This was coupled by appearance of a new band at about 985 cm⁻¹ in H₃PO₄ treated ACs attributed to C-O-C group. This suggested that adjacent carboxylic acid and alcohol groups formed ester linkages upon heating in the presence of an acid. In addition, slight variations in peak shape, intensities and shifts between 1500 and 1000 cm⁻¹ for MACP_{20%}, MACP_{40%} and MACP_{60%} illustrated that the different strengths of phosphoric acid yielded materials of varying surface chemistry.

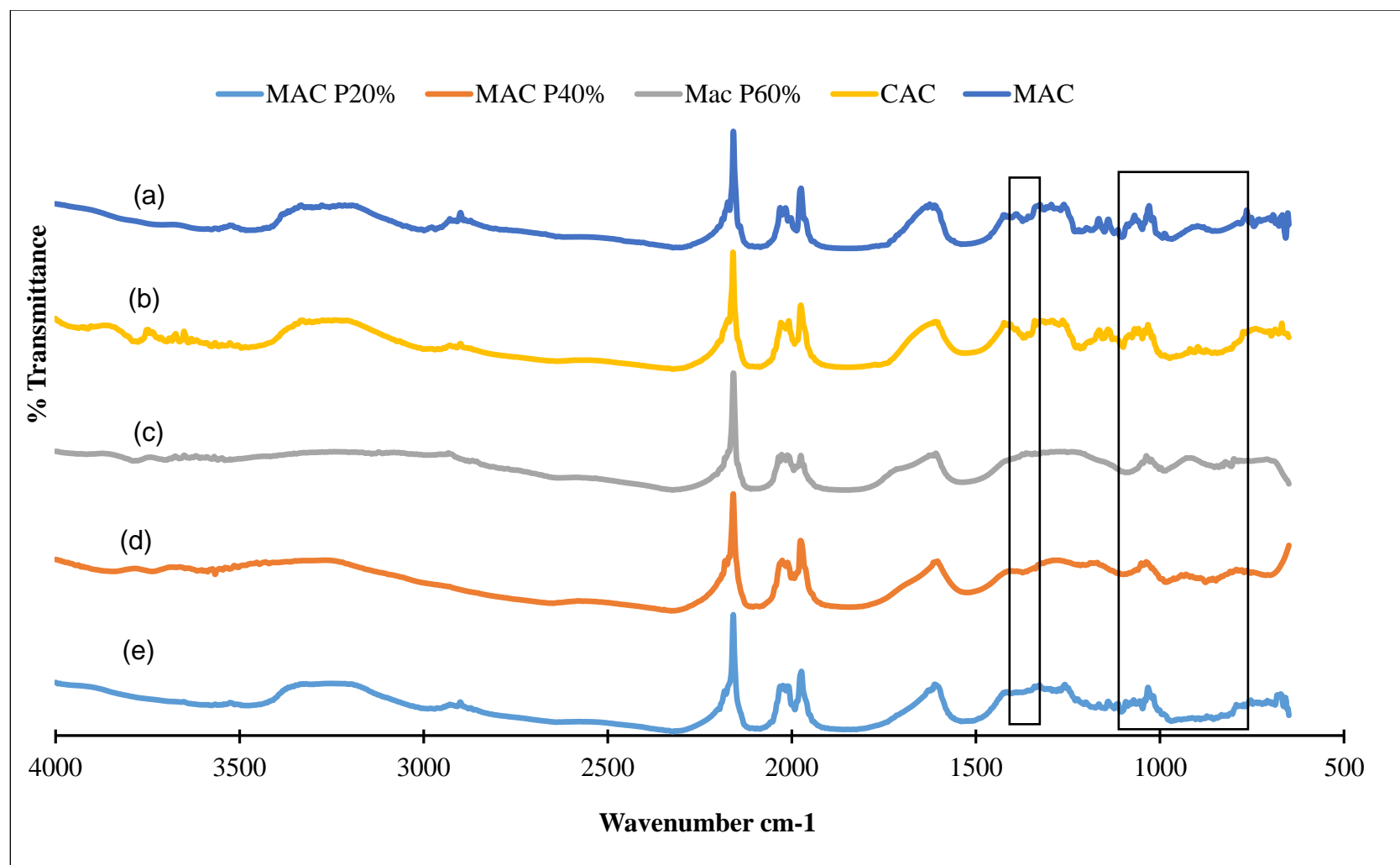
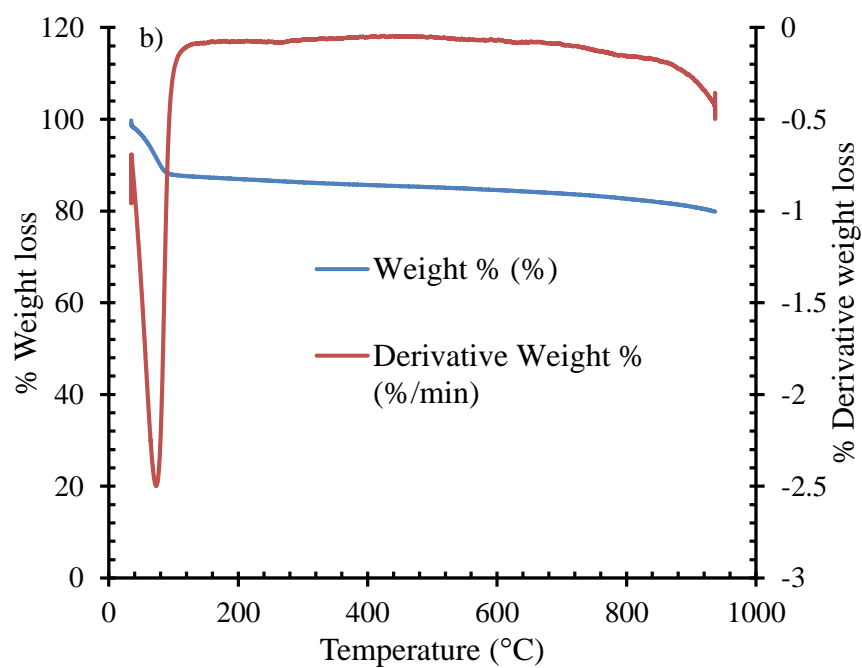
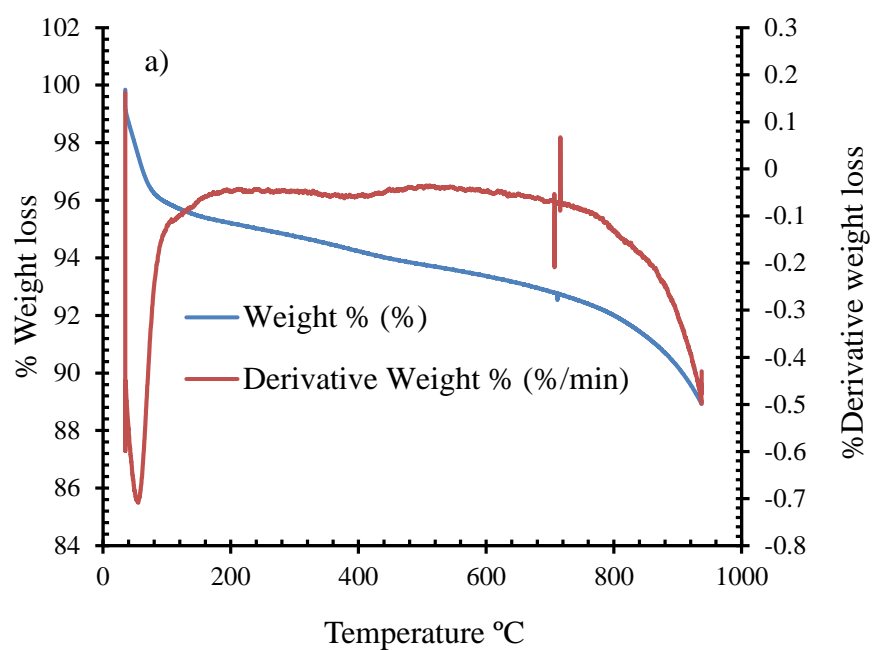


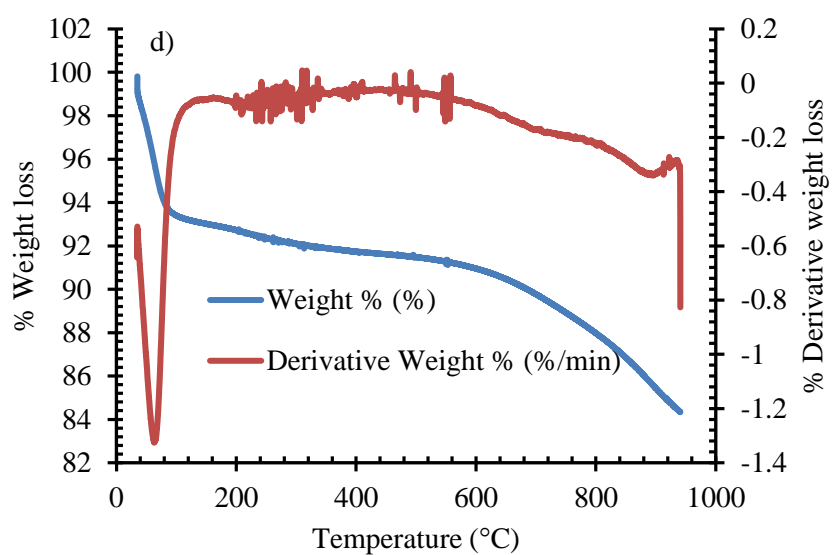
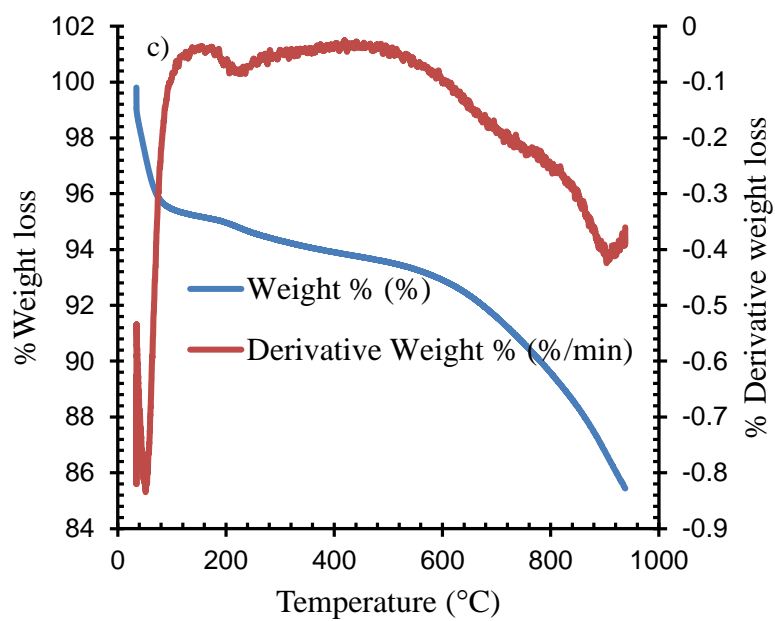
Figure 5.1 FTIR spectra of a) MAC, b) CAC, c) MACP_{60%}, d) MACP_{40%}, e) MACP_{20%},

5.1.1.3 Thermogravimetric analyses

Thermograms of MAC, CAC, MACP_{20%}, MACP_{40%} and MACP_{60%} are illustrated in Figures 5.2 a-e. All TGA thermograms displayed a similar decomposition trend with three weight loss stages. The initial weight loss which is the first step represents weight loss of about (4-6%) in the temperature range 50-150°C. The weight loss observed between 50 and 150°C was assigned to loss of moisture content and this was estimated to 4% for MAC, 6% for CAC, 4.4% for MACP_{20%}, 6.4% for MACP_{40%} and 4.2% for MACP_{60%}.

These results indicated that treatment of MAC with H₃PO₄ increased the moisture content of the resulting carbon probably due to increased oxygenated groups which will then form hydrogen bonds with water molecules. The steep weight loss of about (7-10 %) was observed in a further rise in temperatures between 200-600°C which was assigned to the gasification of volatile organic matter in charcoal. The third weight loss was due to decomposition of AC structure and loss of a strongly bound compound at temperature above 750°C. The functionalized ACs and the coconut AC showed a higher percentage loss compared to the non-modified AC. Similar steps of decomposition were reported in a study done by Gottipati (2012).





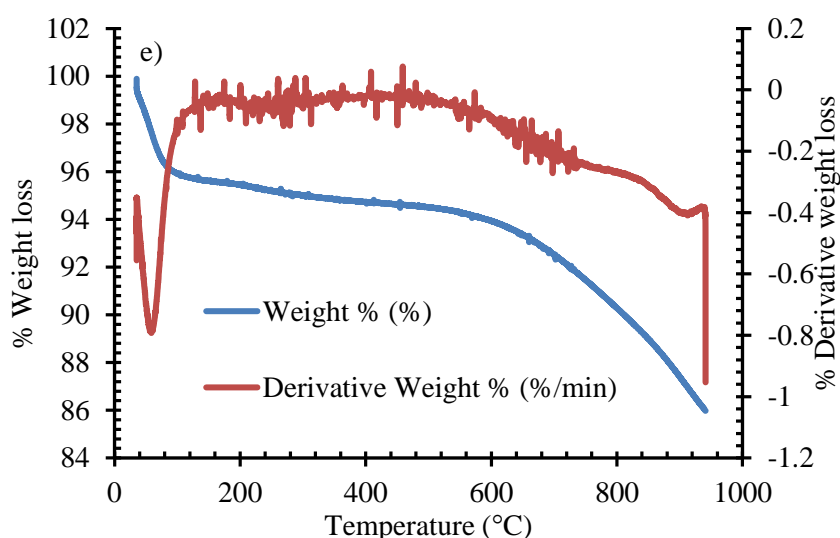


Figure 5.2 Thermographs and derivatives weight loss graphs for CAC a), MAC b), MACP_{20%} c), MACP_{40%} d) and MACP_{60%} e)

5.1.1.4 BET surface area determination

Table 5.2 shows the surface area, pore volume and pore size values for the CAC, MAC and MACP_{60%} materials. MACP_{60%} exhibited the highest BET surface area of 824 m²/g followed by CAC (788 m²/g) and lastly by MAC (545 m²/g). The same trend was observed for the measurements of the single point surface area where the MACP_{60%} was found to have the highest surface area of 919 m²/g followed by CAC with 840 m²/g and lastly MAC with 602 m²/g. The pore volume also followed the same trend and the measurements were found to be 0.494, 0.476, and 0.354 cm³/g for CAC, MACP_{60%} and MAC respectively. The BET surface area values obtained in this study were typical of activated carbon even though they were on the lower range side. ACs are known to possess surface area values ranging from 600-1500 m²/g, but treatment of MAC with 60% H₃PO₄ resulted in material with 824 m²/g surface area.

Table 5.2 BET surface area of various activated carbons

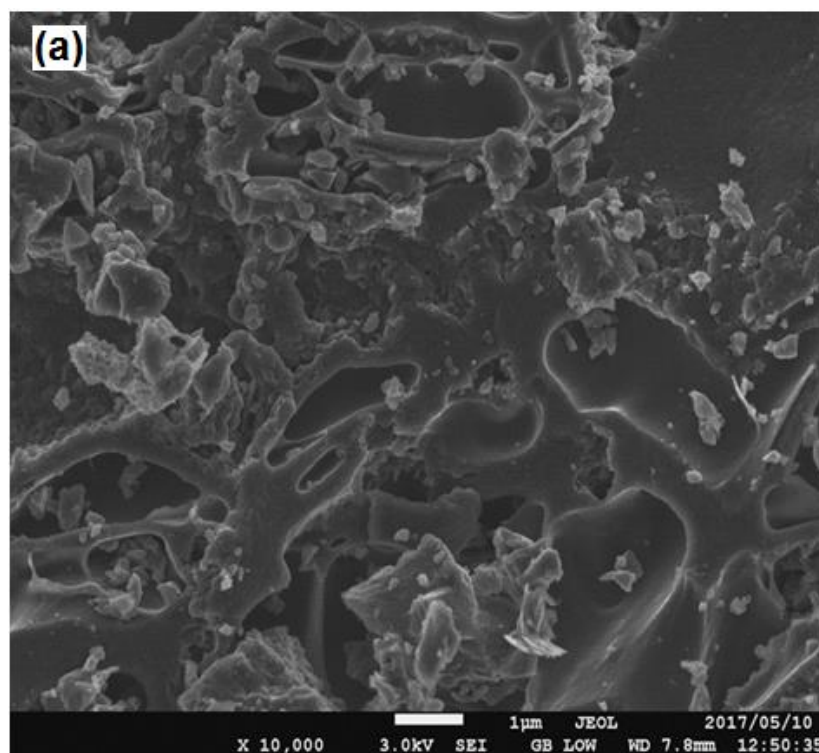
Type of adsorbent	Analysis done		
	BET Surface Area: (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
CAC	788	0.476	2.416
MAC	546	0.354	2.590
MACP _{60%}	824	0.494	2.399

The increase in pore volume observed in MACP_{60%} was attributed to degradation of the carbon structure with subsequent carbonization which causes charring and aromatization of the carbon skeleton leading to creation of the porous structure (El-Hendawy *et al.*, 2001; Olivares-Marin, 2006). The pore size increased with the decrease in surface area, that is, MAC had the highest pore size of 2.590 nm while MACP_{60%} had the lowest pore size value of 2.399 nm. The higher BET surface area and the pore volume, are desirable properties of ACs for effective adsorption (Rosas *et al.*, 2009).

5.1.1.5 SEM analysis of AC

The prepared activated carbons were examined by scanning electron microscope (SEM) to analyse the surface morphology and textural qualities. SEM micrographs of MAC, CAC and MACP_{60%} are presented in Figure 5.3. The pores observed from SEM images have a diameter in micrometer (μm) range. Well-developed porous surface was observed at higher magnification in the CAC and MACP_{60%} which was typical of activated carbon SEM images. It can be seen that there is a huge difference in the morphological characteristics of the *Macadamia* activated carbon before it was treated and after it was chemically treated with phosphoric acid. These

results indicate that treating MAC with phosphoric acid led to the opening of pores. MACP_{60%} displayed similar pore structure to CAC even though CAC seemed to have wider pores. These observations are in agreement with the BET analysis which indicated that MACP_{60%} and CAC had higher surface area than MAC due to their porous nature.



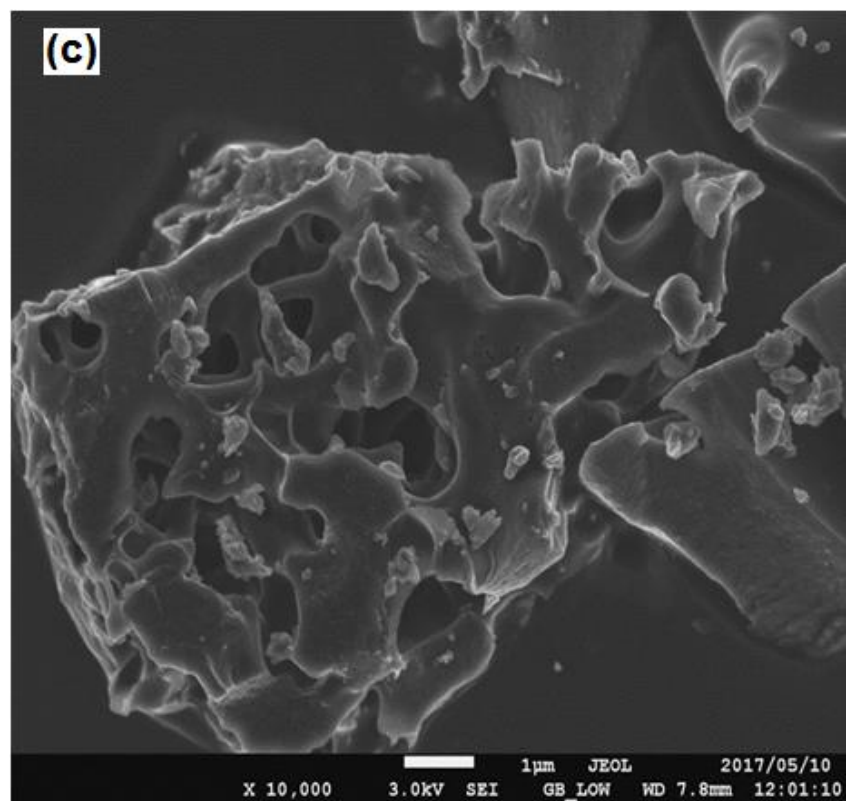
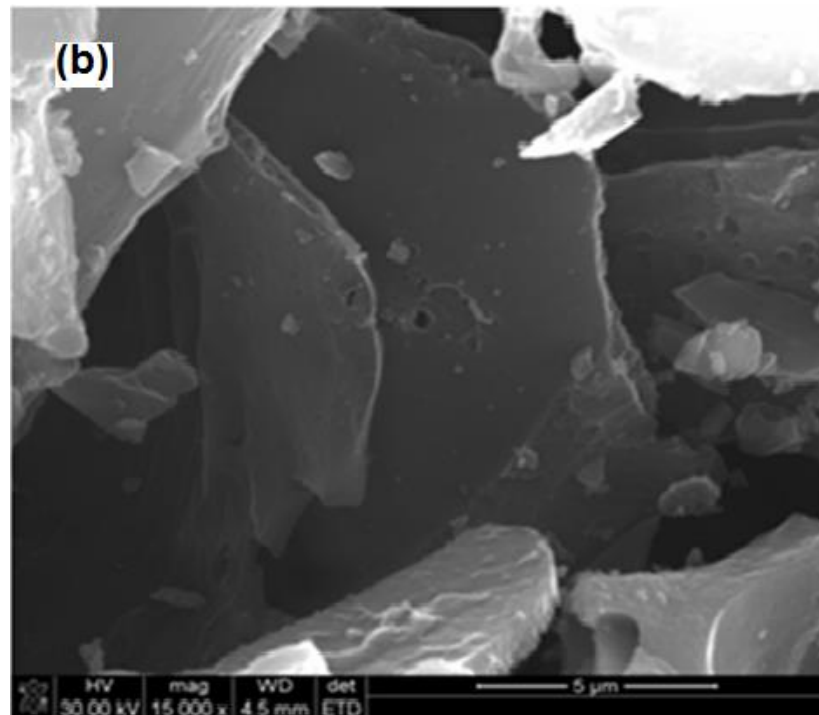


Figure 5.3 SEM images for CAC a), MAC b), and MACP_{60%} c)

5.1.1.6 XRD analysis of ACs

Figure 5.4 shows the X-ray diffraction profiles of CAC, MAC, MACP_{20%}, MACP_{40%} and MACP_{60%}. All the carbon samples exhibited broad peak at 24° which confirmed that the ACs had a predominantly amorphous structure. The observed amorphousness of ACs is actually a good characteristic for porous adsorbents (Tongpoothorn *et al.*, 2011). Broad peaks found at around 24° for all the samples suggested that the ACs were non-graphitized and could exhibit high microporous structure (Zhao *et al.*, 2009). These results were found to be in agreement with the BET results for the phosphoric modified activated carbons. Similar results were also observed in a study that was done by Ramakrishna *et al.* (2012) where activated carbons modified with phosphoric acid were found to be non-graphitized and having a high microporous structure.

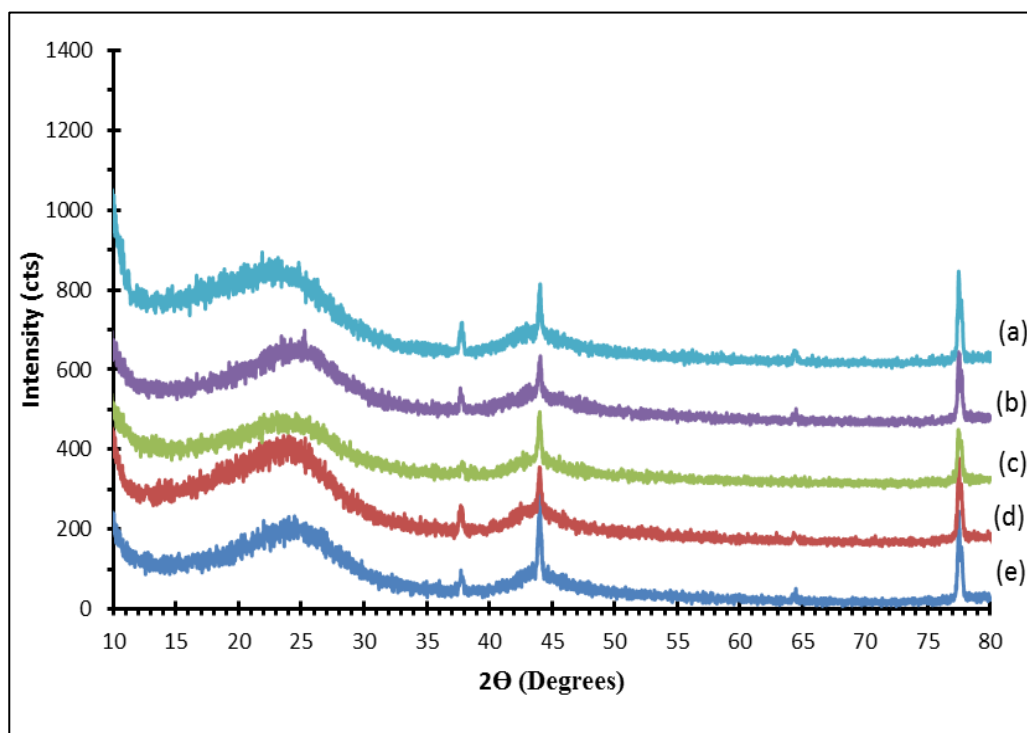


Figure 5.4. XRD patterns for CAC a), MAC b), MACP_{20%} c), MACP_{40%} d) and MACP_{60%} e).

5.1.2 Physical characterization of phosphoric acid modified activated carbons

5.1.2.1 Ash content

Percentage ash content, moisture, volatile matter and attrition results are shown in Table 5.3. The ash content of CAC, MAC, MACP_{20%}, MACP_{40%} and MACP_{60%} was found to be 4.3, 4.7, 6.9, 10.7 and 14.2 % respectively (Table 5.3). It can be observed that the ash content of MAC was slightly higher than that of CAC but increased significantly following treatment with phosphoric acid. The ash content of MAC increased with an increase in concentration of the modifying agent H₃PO₄. Therefore, high ash content could be attributed to the residual of entrapped dehydrated acid products (Girgis *et al.*, 2002). Of the treated carbons only the MACP_{20%} was found to fall within the quality limits specification of ash content.

Table 5.3 Physical properties of phosphoric acid modified activated carbons.

Type of carbon	Moisture (%)	Ash (%)	Volatile %	Attrition %
Quality specification limits for activated carbon	0-15	0-10	0-40	0-2
CAC	0.4	4.3	4.6	0.25
MAC	0.7	4.7	11.7	0.79
MACP _{20%}	3.0	6.9	14.7	3.27
MACP _{40%}	3.4	10.7	15.3	3.51
MACP _{60%}	4.4	14.2	16.3	4.80

5.1.2.2 Moisture content

The moisture content of MAC (0.7%) was closest to that of CAC (0.3%). Modification of MAC with phosphoric acid increased the moisture content of MAC. The moisture content of MACP_{20%}, MACP_{40%}, and MACP_{60%} was 3.0, 3.4, and 4.4%, respectively. Results show that moisture content increased as the

impregnation ratio of modifying agents H_3PO_4 was increased. Madhavakrishnan *et al.* (2008) suggested that no correlation between moisture content and adsorption power of carbon existed. Too much moisture may lead to an incorrect solid-liquid ratio dosages for industrial applications. Although the H_3PO_4 treated AC had higher moisture content compared to the MAC and CAC, it was found to still be within the quality specification limits for activated carbon.

5.1.1.3 Volatile matter

Table 5.3 also shows the volatile content of activated carbons under study. The volatile content of CAC was 4.6% while that of MAC, MACP_{20%}, MACP_{40%} and MACP_{60%} was 11.7%, 14.7%, 15.3%, and 16.3%, respectively. Quality activated carbons may have as high volatile content as 40%. Moreover, the higher the volatile matter the better are its chances of being resistant to attrition. The same trend observed in moisture content and ash content analysis was observed whereby increases in impregnation led to an increase in volatile matter.

5.1.2.4 Attrition Content

The attrition content of MACP_{20%}, MACP_{40%} and MACP_{60%} was found to be higher than 2% which is the quality specification limit for the mining industry. This makes the H_3PO_4 undesirable in the usage on metallurgical plant. This is because these activated carbons will break easily in the carbon in pulp circuit leading to them being sieved through together with the residue material. This will result in the loss of gold as these fine particles will be lost to the waste dams and fine particles of carbon are known to adsorb gold quicker than the granules carbon due to improved surface area.

5.1.3 Optimization of adsorption parameters for gold cyanide uptake

5.1.3.1 Effect of adsorbent dose

The results obtained from the optimization of activated carbons sorbent dosage for gold adsorption are showed in Figure 5.5. In all materials, the gold adsorption rate increased steeply from 1 to 3 g and seemed to slow down from 3 to 4 g as it reached saturation. It is known that free sorption surface and adsorption sites increase as sorbent dosage is increased. This may lead to an increase in number of available active adsorption sites for the same number of moles of gold species. As a result, 4 g was regarded as optimum sorbent dosage even though there was still an increase in the adsorption rate for gold. Therefore, in the succeeding studies 4 g of activated carbons were used. The adsorption efficiency increase in the order $MAC < MACP_{20\%} < MACP_{40\%} < MACP_{60\%} < CAC$. Nonetheless, the treatment of MAC with increasing concentrations of H_3PO_4 produced an AC that was getting closer to the quality of CAC in terms of gold adsorption mass of adsorbent. Similar observation of increasing percentage adsorption with increase in sorbent dosage have been made by numerous researchers.

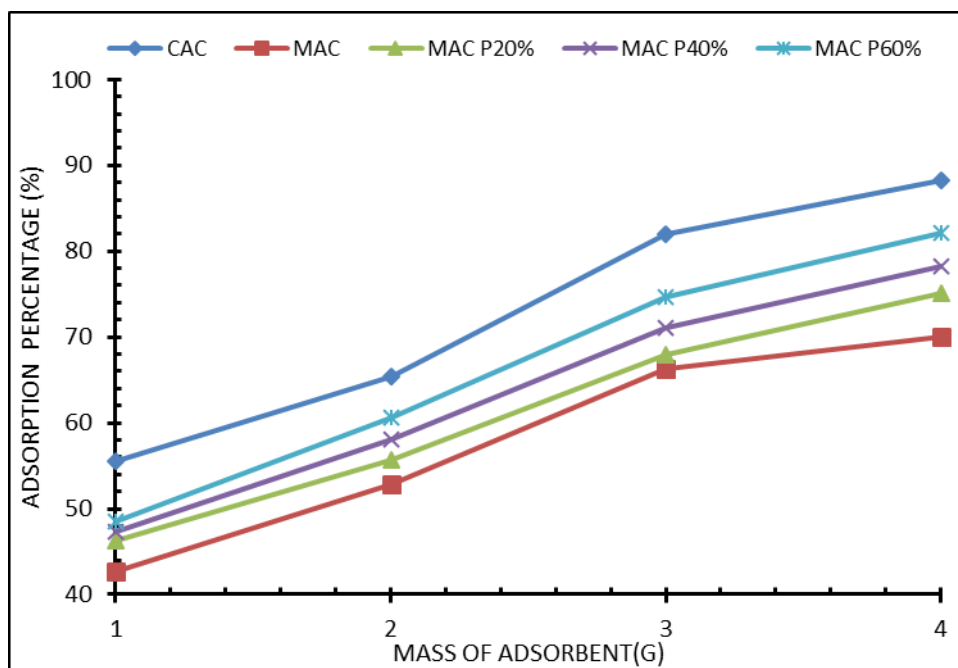
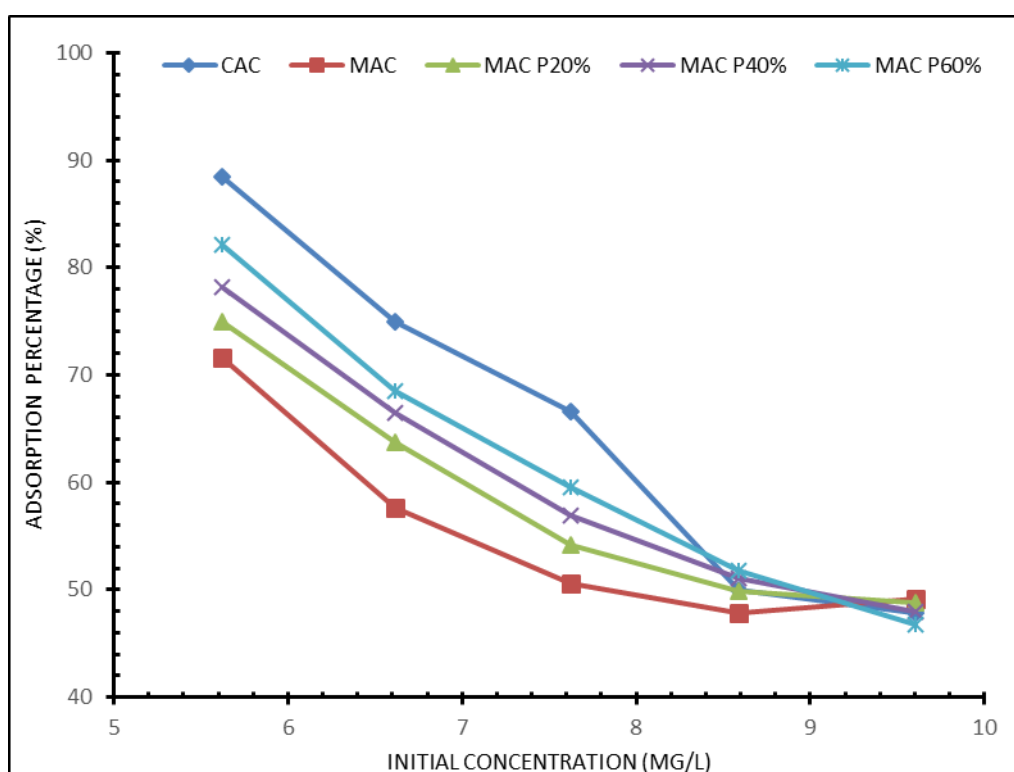


Figure 5.5 Effect of dose of adsorbent on gold adsorption. Solution pH 10; solution volume, 1000 mL; contact time, 1 h; agitation speed used 150 rpm and initial concentration of solution, 5.622 mg/L.

5.1.3.2 Effect of initial concentration

Optimization of gold initial concentration as a function of percentage adsorption is illustrated in Figure 5.6a. All adsorbents under investigation exhibited a similar trend. A decrease in the percentage of the removal of gold was observed as the initial gold concentration in the solution was increased from 5.5 to 9.5 mg/L. This was due to the fact that at lower concentration, the ratio of the initial moles of gold species to the available adsorption sites was low and subsequently the fractional adsorption became independent of initial concentration. While, at higher concentration the available adsorption sites for adsorption become fewer compared to the moles of gold species present and hence the percentage removal of gold was dependent on the initial gold concentration. On the other hand an increase in the initial concentration of gold led to an increase on the adsorption capacity of gold on activated carbon.

This showed that the initial gold concentration played an important role in the adsorption capacity of gold on activated carbon. A maximum adsorption of gold was seen at 5.5 mg/L in which it was observed from all the investigated carbons. The adsorption percentage ranged from 70% to 90% and the specific adsorption percentages were 70%, 74%, 76%, 82% and 91% for MAC, MACP_{20%}, MACP_{40%}, MACP_{60%}, and CAC, respectively. Again the same trend in terms of adsorption efficiency was observed at lower concentrations where CAC showed highest removal followed by MACP_{60%}, MACP_{40%}, MACP_{20%}, MAC in that order. That is, modified MAC performed better than its pristine form signifying the importance of secondary treatment in ACs. For subsequent experiments 5.5 mg/L was used because of higher adsorption efficiency achieved by all adsorbents on this concentration.



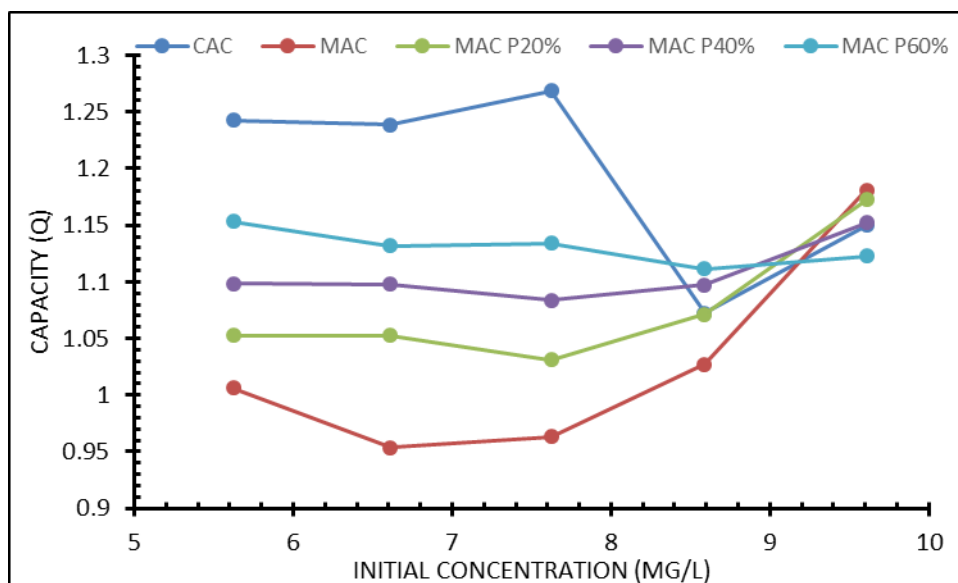


Figure 5.6 Effect of initial concentration of gold on gold adsorption. a) rate of adsorption and b) adsorption capacity. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, agitation speed used 150 rpm and dosage of carbon, 4 g.

5.1.3.3 Effect of agitation speed

The effect of shaking speed on the adsorbent/adsorbate system was investigated by varying the agitation speed from 50-250 rpm whilst other parameters were kept constant and the results are showed in Figure 5.7. The adsorption percentage was found to increase rapidly from 50-150 rpm then slowed down almost reaching equilibrium between 200-250 rpm. It was observed that some of the carbon remained at the base of the bottle when the samples were agitated below 150 rpm implying less contact between adsorbent and adsorbate and at 200-250 rpm the bottles were shaking vigorously leading to spillages. The optimum shaking speed was found to be 200 rpm but to avoid spillages in the succeeding studies only 150 rpm speed was used.

The observed increase in the percentage of adsorption of gold with shaking speed can be assigned to the improvement in contact between the gold species in solution

and the active sites on the carbons, thereby promoting effective transfer of adsorbate ions to the adsorbent site. Similar results were obtained in a study done by Soleimani *et al.* (2008) in which an increase in agitation speed led to an increase in gold adsorption. MACP_{60%} was again found displaying the highest adsorption percentage compared to other MAC samples but it was still lower than that of CAC. The order of percentage adsorption increased according to the following trend $MAC < MACP_{20\%} < MACP_{40\%} < MACP_{60\%} < CAC$. As a result, it can be observed that the functionalization of MAC with phosphoric acid improved its adsorption percentage for gold ions.

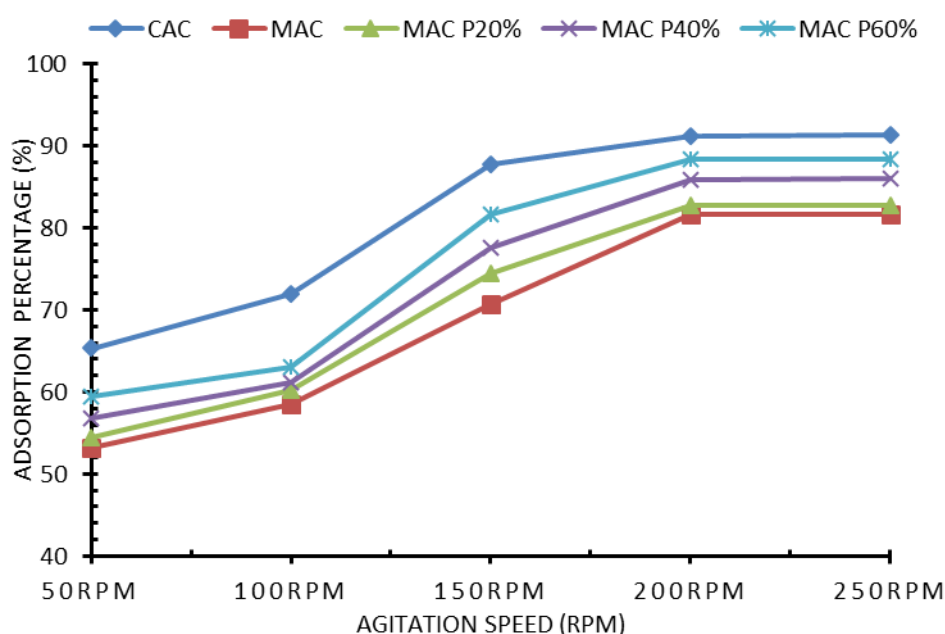


Figure 5.7 Effect of initial agitation speed on gold adsorption. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g and concentrations used were 5.7 mg/L.

5.1.3.4 Effect of contact time

Figure 5.8 shows the results obtained from varying the time during gold adsorption. It was observed that the percentage adsorption of gold ions from solution increased steeply as the time of agitation was increased from 1 to 4 h, for all adsorbents except

MAC. From 4 to 6 h, the adsorbents seemed to have reached equilibrium. MAC reached equilibrium between 5 to 6 h. The observed rapid increase in percentage adsorption was initially because of the adsorption sites being more available for the adsorbent-adsorbate interactions, resulting in higher adsorption rate. However, the functional groups started to get saturated as the time increased beyond 5 h resulting in lower adsorption rates and consequently equilibrium being reached. A similar trend observed in the preceding studies whereby the order of adsorption below 2 h was similar to the study of dosage, concentration and agitation speed effects was noted.

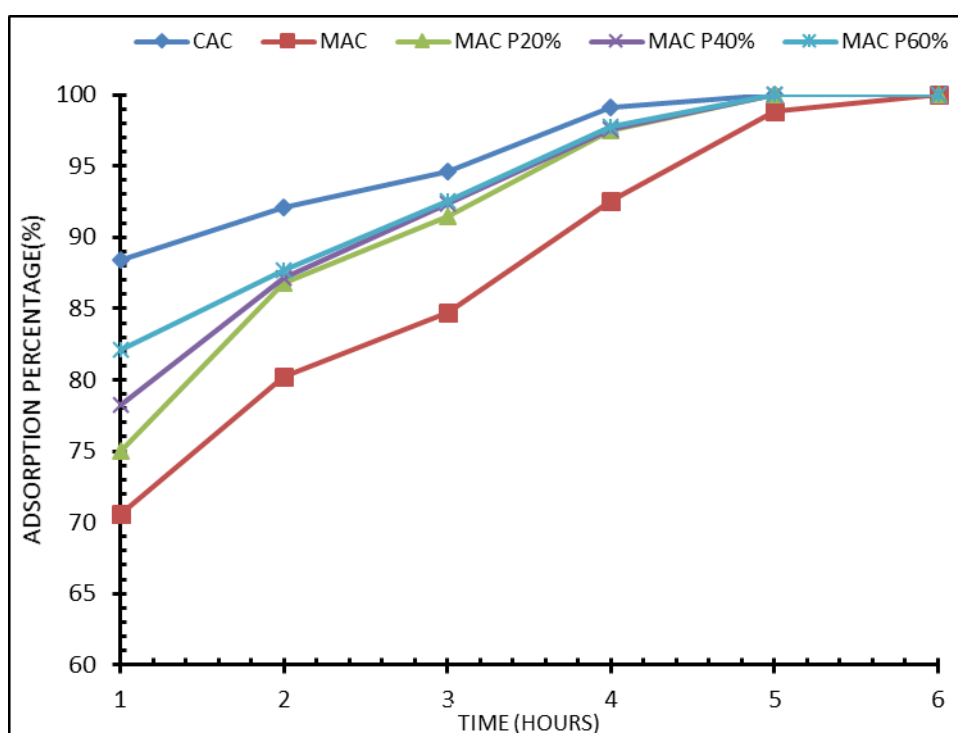


Figure 5.8 Effect of time on gold adsorption. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g, agitation speed used 150 rpm and concentrations used were 5.7 ppm.

The MAC had the lowest adsorption followed by MACP_{20%}, MACP_{40%}, MACP_{60%}, and CAC. After 5 h all the carbons seemed to attain similar adsorption efficiency and 6 h was regarded as the optimum time. The longer equilibration time observed for pristine MAC compared to the modified MACs could be attributed to the inaccessibility of MAC adsorption sites due to the closure of pores (Table 5.2, lesser pore volume). SEM also revealed that modified MAC had improved pore structure than virgin MAC.

5.1.3.5 Selectivity studies on adsorption of gold (effect of interfering species)

Metal ions that have similar or less ionic radii size as the gold ion were chosen for selectivity studies. The metal ions selected were nickel (Ni: Aw 58.69 g/mol: ionic radius 69 pm), lead (Pb: Aw 65.39 g/mol: ionic radius 74 pm), iron (Fe: Aw 55.85 g/mol: ionic radius 64 pm), and copper (Cu: Aw 63.55 g/mol: ionic radius 72 pm). These metal ions were likely found to coexist with gold in the ore. The selectivity of the activated carbons was tested using a mixture of 4 metal ions in solution together with gold ions of about 6 mg/L solution containing Pb, Ni, Fe Cu and Au. The experiments were done under optimum conditions of: time 6 h, pH 10, adsorbent mass (4 g), 1000 mL solution volume and agitation speed of 150 rpm. The concentration of the unadsorbed metal ions was determined by AAS. The results are shown in Table 5.4. About 64% adsorption was achieved for MAC, 61% for MACP_{20%}, 61% for MACP_{40%}, and 63% for MACP_{60%}, and 80% for CAC.

From the results, it can be observed that none of the activated carbons reached 100% adsorption percentage, and this indicated that the presence of other metal ions lowered the percent adsorption of gold. The order of selectivity from the examined metals displayed a similar trend to other experiments found in the

literature on adsorption percentage with nickel being found to interfere the most while copper interfered least for all the activated carbons investigated. Sayiner *et al.* (2013) investigated the effect of silver, nickel and copper cyanides on gold adsorption by activated carbons from leached samples. It was also observed that nickel had a high percent adsorption as compared to the Cu which had the lowest. This observation was assigned to the fact that Ni(CN)_4^{2-} complex has 4 CN^- ions compared to 2 CN^- in Ag(CN)_2^- which resulted in higher hydration. Thus, it was better dispersed in the solution without forming clusters which enabled the adsorption on activated carbon (Yin *et al.*, 2011).

Table 5.4 Effects of competing ions on gold adsorption

Metals ions	<i>Percentage adsorption for the activated carbons (%)</i>				
	CAC	MAC	MACP _{20%}	MACP _{40%}	MACP _{60%}
Copper	3.95	6.67	9.09	5.39	8.67
Iron	4.26	17.21	8.22	5.79	4.41
Nickel	22.52	21.27	20.71	22.50	24.45
Lead	16.52	14.53	18.61	19.46	17.80
Gold	80.76	64.24	60.83	60.96	62.82

5.1.3.6 Reusability of H_3PO_4 activated carbon

The results so far have demonstrated that MACP_{60%} had better adsorption percentage for gold ion than other phosphoric acid modifications. Therefore, the reusability studies were carried out using MACP_{60%}, MAC and CAC for comparison. The results obtained from the investigation of ACs reusability potential are displayed in Figure 5.9. It can be observed that the percentage adsorption of CAC in the first cycle was 87%, and then it decreased to 83% in the fifth cycle. On the other hand, the percentage adsorption of MACP_{60%} was 77% in the first cycle and decreased to 67% in the fifth cycle. MAC showed the lowest

percent adsorption of 70% in the first cycle and 65% in the fifth cycle. Even though MACP_{60%} exhibited lower percent adsorption than CAC, adsorption percentage above 65% is regarded as satisfactory. Therefore, MACP_{60%} showed satisfactory adsorption percentage toward gold ion with loss of efficiency of only about 10% in five cycles of adsorption and desorption.

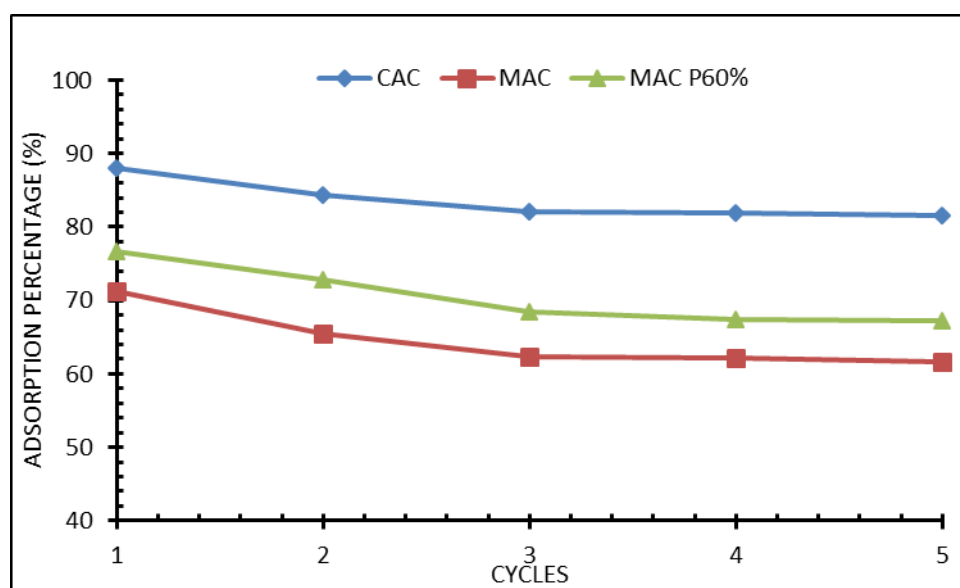


Figure 5.9 showing re-usability of the activated carbons. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4g, agitation speed used 150 rpm and concentrations used were 5.7 mg/L.

5.1.3.7 Application of H_3PO_4 modified activated carbons on real sample

Barren samples were collected from West Wits Chemical Lab in western deep levels Carletonville that is part of the Witwatersrand Basin in Johannesburg, South Africa. A Barren sample is a solution from the smelt house from which gold has been removed during a hydrometallurgical treatment. It is often recycled back to the plant to be re-used in the process. The sample was analysed and found to contain residual Au at low concentration of 5.876 mg/L, Ni (97.800 mg/L), Cu (5.799 mg/L), Fe (4.12 mg/L) and (Pb 1.113 mg/L). The concentration of the unabsorbed gold species in real samples was determined by AAS and the results

are displayed in Figure 5.10. About 57% adsorption was achieved for MAC and 65% for MACP_{60%} and 74% for CAC.

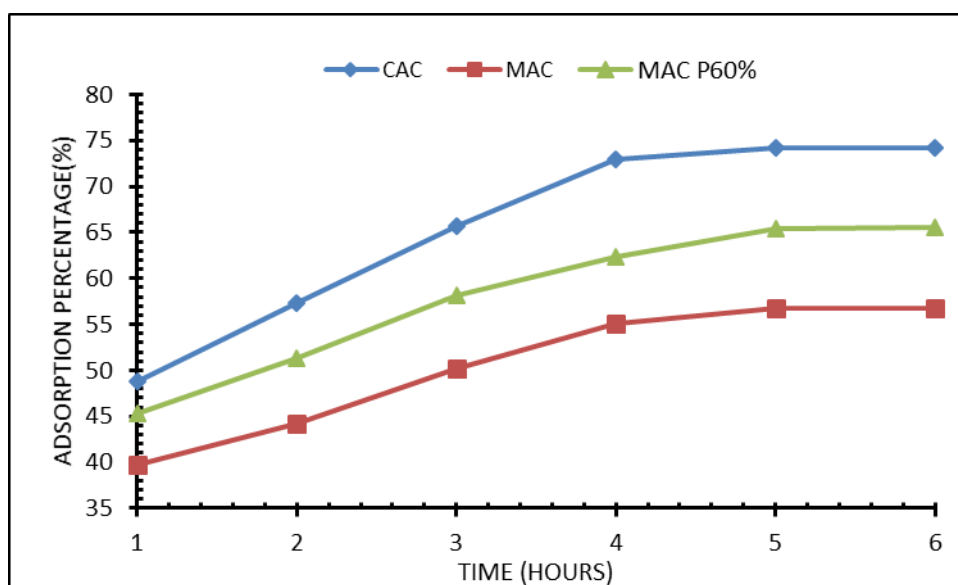


Figure 5.10 Application of ACs on real world samples. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g, agitation speed used 150 rpm and the initial concentrations measured were Au=5.876 Ni=97.8, Fe=4.12, Cu=5.799 and Pb=1.113 mg/L.

5.1.3.8 Adsorption isotherms for H_3PO_4 ACs

An equilibrium isotherm is a mathematical expression relating the concentration of the adsorbate in the liquid phase with the concentration of the adsorbate on the adsorbent at constant temperature. The Langmuir and Freundlich models were used to study the adsorption of gold cyanide ion on the AC and the results are displayed on Table 5.5. The Langmuir model was first developed to describe the vapour adsorption on homogeneous surfaces (Langmuir 1918). However, when used for solid-liquid systems several assumptions have to be made. These assumptions are: number of surface adsorption sites is fixed, adsorption involves a single monolayer, adsorption behaviour is independent of surface coverage and all adsorption sites

are represented by similar types of functional groups. The linearized Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{bQ_o} \dots\dots\dots (5.1)$$

Where, q_e is the amount of solute adsorbed on the surface of adsorbent (mg/g), C_e is the equilibrium gold cyanide concentration (mg/mL), Q_o is the saturated monolayer adsorption capacity (mg/g), and b is the Langmuir adsorption constant (L/mg). A plot of C_e/q_e versus C_e gives the values of Q_o and b (Wang *et al.*, 2009). Freundlich adsorption isotherm which assumes a multilayer adsorption can be given by the linearized form:

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \dots\dots\dots (5.2)$$

Where, K_F is the Freundlich constant, and n is the Freundlich exponent. The experimental values for q_{exp} and q_{max} are comparable. The summary of the results obtained by fitting the experimental data to the two models is supplied in Table 5.5. using the coefficient of determination error terms (R^2), it can be observed that the ACs followed different removal mechanisms. CAC fitted Freundlich ($R^2=0.936$). MACP_{20%} and MACP_{40%} were better described by the Langmuir fit while MACP_{60%} followed Freundlich multilayer adsorption. The same mechanism displayed by CAC and MACP_{60%} could probably be the reason why MACP_{60%} showed closer percentage adsorption of gold ion to CAC compared to MACP_{20%} and MACP_{40%}. Increased n values indicated a rapid adsorption of Au on activated carbon. Similar results were observed from a study done by Sayiner *et al.* (2013).

Table 5.5 Langmuir and Freundlich adsorption isotherm for H₃PO₄

Adsorbents	Langmuir			Freundlich		
	Q _m	b	R ²	K _F	n	R ²
CAC	10.86	102.04	0.94	5.81	5.08	0.96
MAC	3.28	52.11	0.93	4.17	2.54	0.91
MACP _{20%}	4.83	58.28	0.93	4.53	2.84	0.95
MACP _{40%}	5.78	64.55	0.95	4.85	3.21	0.97
MACP _{60%}	6.7	71.03	0.97	5.21	3.58	0.96

5.1.3.8 Kinetic models for H₃PO₄ ACs

Data from the effect of contact time was fitted in the kinetic model to evaluate the process of adsorption and the results are given in Table 5.6. Two most commonly used rate models were investigated, pseudo-first-order and pseudo-second-order. These models were used in their linearized form of, Eq. 5.3 and 5.4 respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots \dots \dots (5.3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots \dots \dots (5.4)$$

Where k₁ (1/min) is the pseudo-first-order rate constant of the adsorption process and k₂ (g/mg/min) is the pseudo-second-order rate constant, q_t (mg/g) is the amount of Au(CN)₂⁻ adsorbed at any time t. The values of q_e and k₁ were calculated from linearized form of equation 5.3. The slope and intercept from a graph of t/q_t vs t were used to calculate q_e and k₂, respectively. From the graphs, it was observed

that correlation coefficient values R^2 of the pseudo-second order kinetics produced better quality of linearization compared to the pseudo-first order kinetics. The pseudo-second order gave adsorption data giving R^2 values that are very close to 1. This meant that adsorption of $\text{Au}(\text{CN})_2^-$ onto activated carbon was more of a chemisorption.

Table 5.6 Kinetic models constants for H_3PO_4 AC

Kinetic Models	Parameters	CAC	MAC	MACN _{20%}	MACN _{40%}	MACN _{55%}
Pseudo-first order	k_1 (min)	0.0168	0.0158	0.01737	0.01721	0.01699
	q_e (cal)					
	(mg/g)	0.900	1.814	1.488	1.380	1.265
	R^2	0.963	0.907	0.969	0.969	0.965
Pseudo-second order	k_2					
	(g/mg/min)	0.1026	0.0311	0.04716	0.05376	0.06211
	q_e (cal)					
	(mg/g)	1.429	1.457	1.454	1.448	1.441
	R^2	0.999	0.988	0.996	0.997	0.997

5.2 Modification of *Macadamia* activated carbons with nitric acid

Following similar protocol that was used for H_3PO_4 modification, three adsorbents modified with three different concentrations of HNO_3 were obtained. The adsorbents were given the following acronym MACN_{20%}, MACN_{40%} and MACN_{55%} corresponding to 20% v/v, 40% v/v and 55% v/v concentrations of nitric acid activating agent. The following subsection will discuss the characterization and adsorption studies of these adsorbents.

5.2.1 Instrumental characterization of HNO₃ modified activated carbons

5.2.1.1 Elemental analysis

The percent carbon, hydrogen, nitrogen, sulphur and oxygen content for studied ACs is shown in Table 5.7. The treatment of MAC with various concentrations of HNO₃ resulted in improved carbon content. The increase in carbon content was attributed to the removal of oxygenated functional groups during modification. The percentage carbon of MAC increased from 83.27% to 87.68% following treatment with 55% (v/v) nitric acid. This accumulated to about 5% increase. Sharifan (2014) noted that the increase in carbon content following carbonization was an indication of non-carbon elements being released during pyrolysis. The C content of the MACN_{55%} was also found to be closer to that of CAC with just a difference of about 1.5%. The oxygen content calculated by difference decreased as HNO₃ concentrations increased.

Table 5.7: Elemental analysis of ACs

Type of carbon	CHN analysis (%)				
	C	H	N	S	O*
CAC	89.05	<0.1	0.17	<0.1	10.78
MAC	83.27	1.53	0.50	<0.1	14.70
MACN _{20%}	86.3	1.05	0.19	<0.1	12.46
MACN _{40%}	86.61	1.30	0.52	<0.1	11.57
MACN _{55%}	87.68	<0.1	<0.1	<0.1	12.32

*computed by difference

5.2.1.1 FTIR Spectra of various activated carbons

Figure 5.10 shows the FTIR spectra of CAC, MAC, MACN_{20%}, MACN_{40%} and MACN_{60%}. The FTIR spectra were found to not differ a lot due to similar chemical

functionalities of ACs. However, some of differences or changes (peak shifts and appearance of new peaks) as demonstrated by the markings at around 3500 cm^{-1} , 1400 cm^{-1} and 1000 cm^{-1} were observed. Specifically, a broad band at 3400 cm^{-1} assigned to OH^- of alcohols was observed in MAC and CAC. The band is assigned to bonded and non-bonded hydroxyl groups in treated MAC, particularly $\text{MACN}_{55\%}$. In addition MAC and CAC exhibited a signal located at 1374 cm^{-1} and 1366 cm^{-1} , respectively attributed to the C=O vibration of carboxylate group. Another notable change in the spectra is the presence of C-O-C band at 987, 985, and 982 cm^{-1} in $\text{MACN}_{20\%}$, $\text{MACN}_{40\%}$ and $\text{MACN}_{55\%}$, respectively. The absence of clear OH^- and carboxylate functional groups in nitric acid treated MAC, coupled with presence of new ester bands suggested that there was a nucleophilic acyl substitution reaction that produce esters on the surface of ACs. Furthermore, the fact that the new C-O-C bands occurred at different wavenumbers implied that they were in different chemical environments.

Therefore, one can conclude that the surface chemistries of $\text{MACN}_{20\%}$, $\text{MACN}_{40\%}$ and $\text{MACN}_{55\%}$ were different to one another and to that of MAC signifying a successful modification.

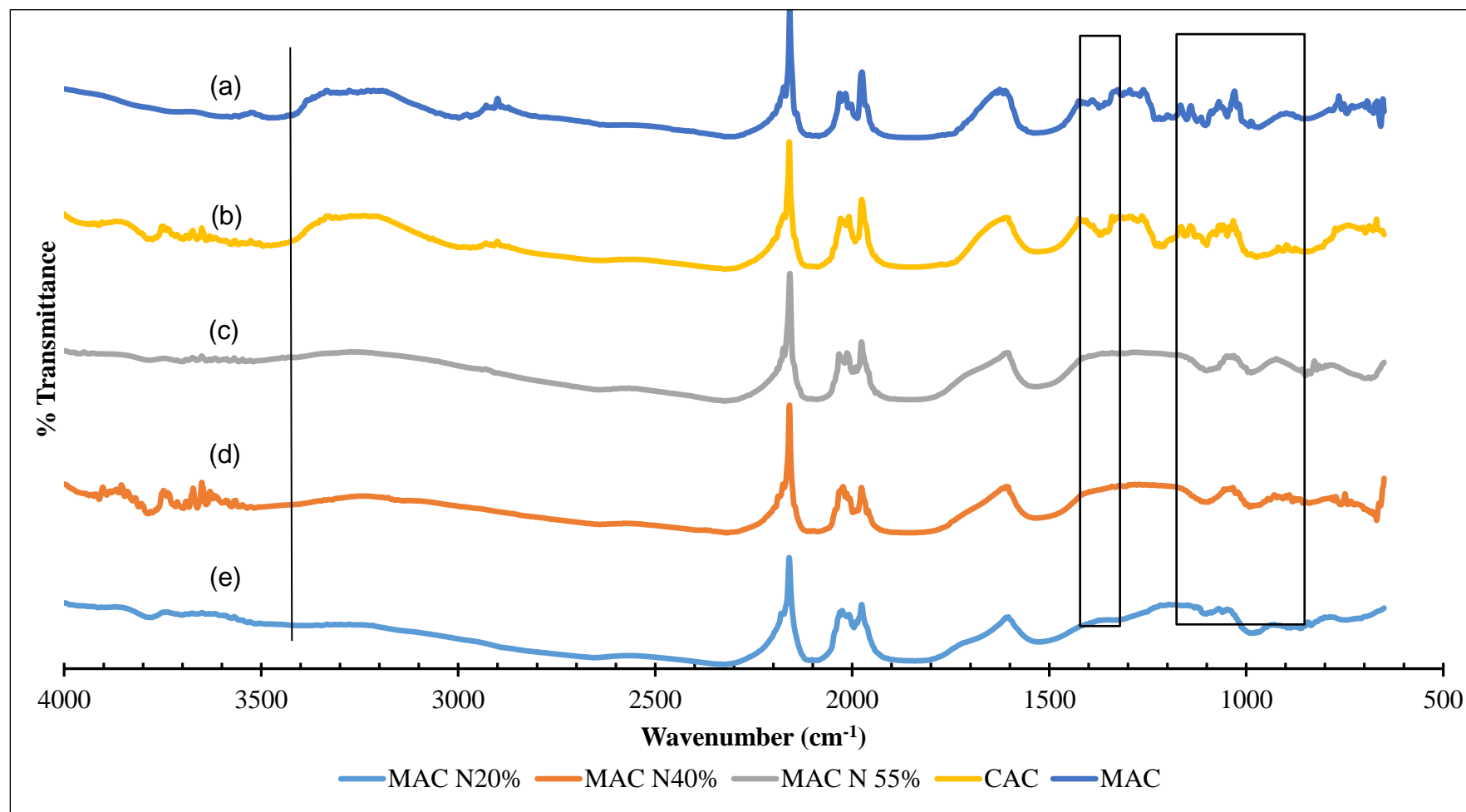
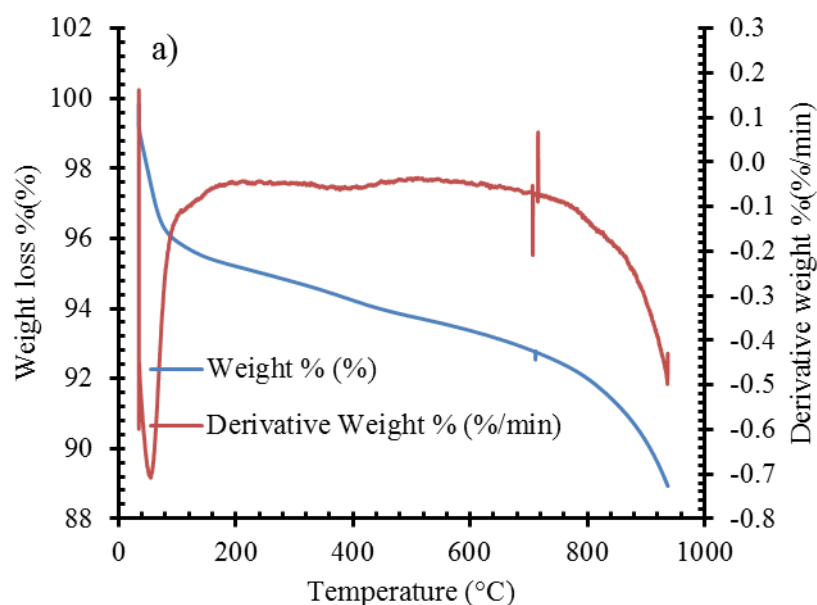
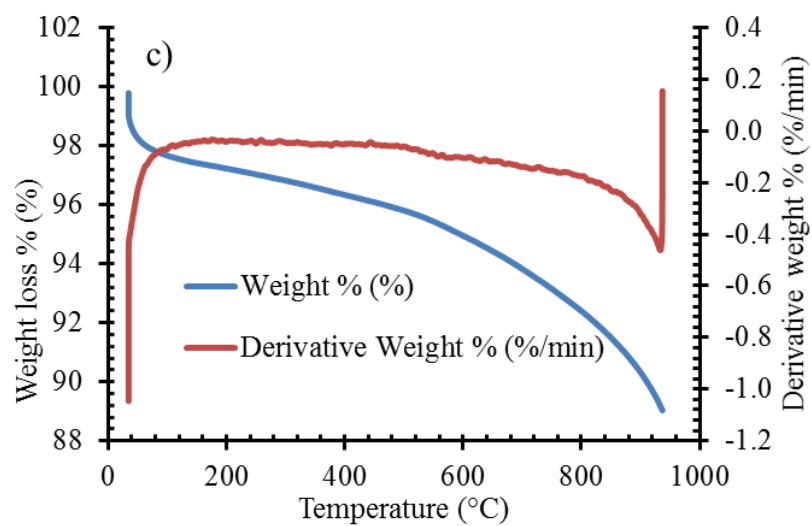
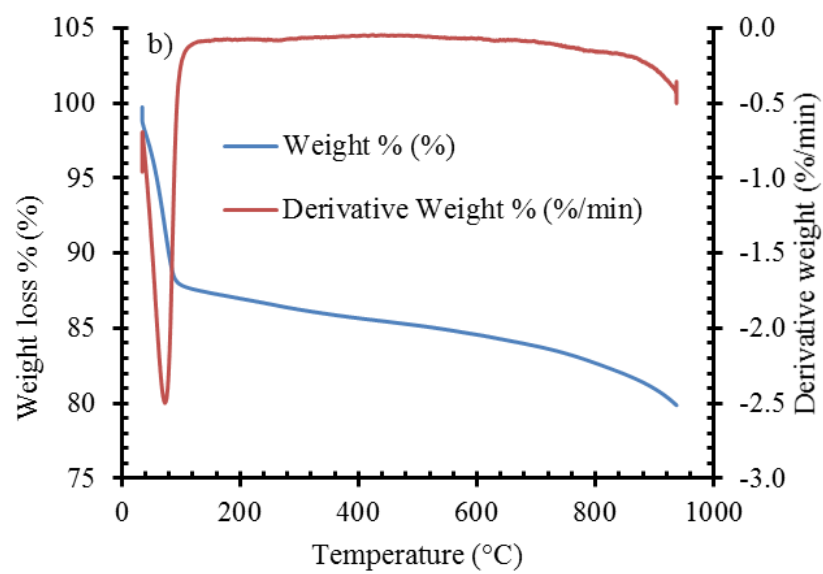


Figure 5.11 FTIR spectra of MAC (a), CAC (b), MACN_{55%} (c), MACN_{40%} (d) and MACN_{20%} (e) adsorbents.

5.2.1.3 Thermogravimetric analyses

Thermogravimetric analyses were conducted to determine the decomposition patterns of AC samples. Thermograms and differential curves are depicted in Figure 5.12 a-e. All samples showed a weight loss at about 100°C which accounted for the loss of moisture. The estimated moisture contents were 4%, 10%, 2%, 8%, and 4% for CAC, MAC, MACN_{20%}, MACN_{40%} and MACN_{55%}, respectively. The second decomposition stage observed between 200-600°C was ascribed to the loss of compounds organic matter of ACs. The final decomposition stage observed beyond 750°C was attributed to the loss of strongly attached organic compounds within the carbon matrix such as lignin. The functionalized ACs and the CAC showed a high percentage loss compared to the MAC.





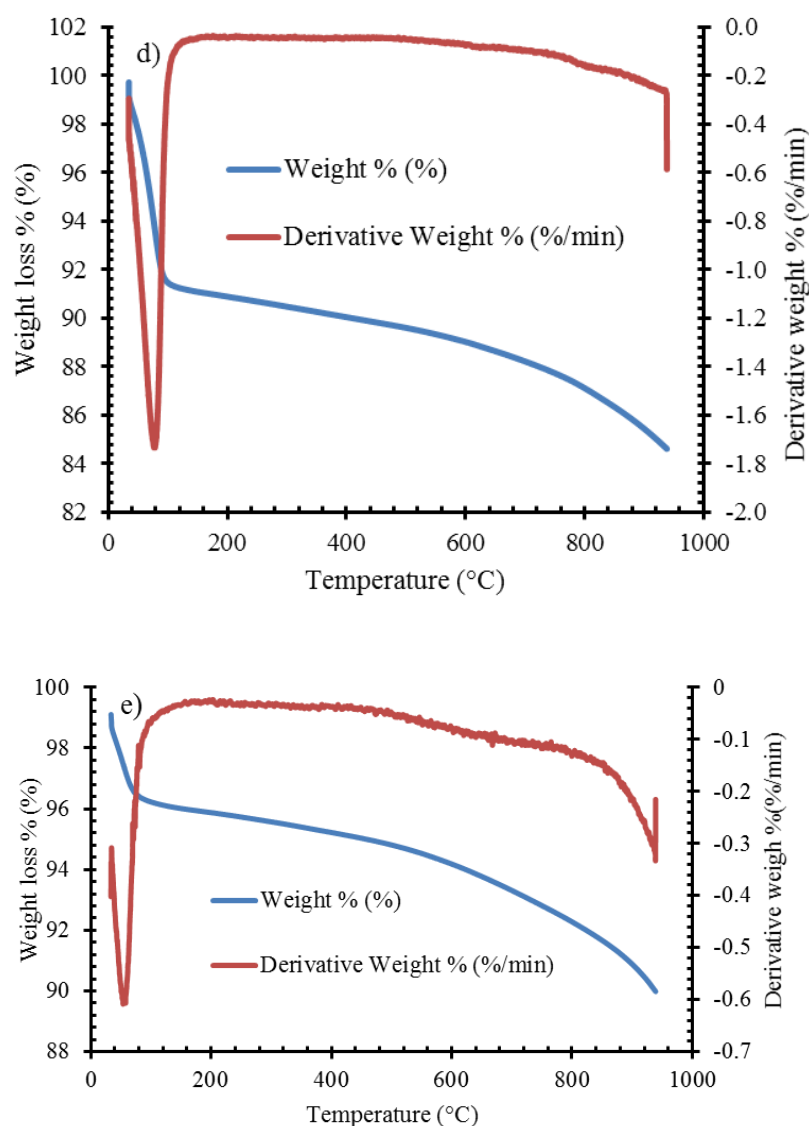


Figure 5.12 Thermograms and derivative weight loss graphs for CAC a), MAC b), MACN_{20%} c), MACN_{40%} d) and MACN_{55%} e) adsorbents.

5.2.1.4 BET surface determination of various carbons

The surface area, pore volume, and pore size of CAC, MAC and MACN_{55%} are illustrated in Table 5.8. CAC had the highest BET surface area of 788 m²/g but treatment of MAC with 55% HNO₃ increased the surface area from 545 to 748 m²/g a value that was closer to that of CAC. *Macadamia* based activated carbons have been reported in literature to have BET surface area ranging from 600-1500 m²/g (Pezoti *et al.*, 2013, Dejang *et al.*, 2015).

The pore volume of pristine MAC increased from 0.354 cm³/g to 0.489 cm³/g which was very close to 0.476 cm³/g for CAC. The closeness of CAC to MACN_{55%} BET surface area and pore volume values suggested that the two activated carbons have similar physical characteristics. That is, treatment of MAC with 55% v/v concentrated nitric acid produced a carbon with similar physical attributes to CAC. Pore size of all three tested activated carbons were in the same range. The increase in surface area following treatment of ACs, produced from different precursors, with nitric acid has been observed by other researchers (Vasu 2008, Yavuz *et al.* 2014, Lopes *et al.*, 2015).

Table 5.8 BET surface area of selected activated carbons (HNO₃)

Type of adsorbent	BET Surface Area: m ² /g	Pore Volume cm ³ /g	Pore Size nm
CAC	788	0.476	2.416
MAC	546	0.354	2.59
MACN _{55%}	748	0.489	2.613

5.2.1.5 XRD of selected activated carbons (HNO₃)

The X-ray diffraction patterns for CAC, MAC, MACN_{20%}, MACN_{40%} and MACN_{55%} are depicted in Figure 5.13. The AC samples were found to have both broad peaks and few sharp peaks which revealed a predominantly amorphous structure. Zhao *et al.* (2009) pointed out a link between porous structures of adsorbents and their amorphous structure which could be ideal for adsorption. Similar to ACs modified with H₃PO₄ stand out peaks were observed at 2θ= 24°, 37°, 44° and 77°. Broad peaks were also observed at around 24° for all the nitric modified activated carbons just as it was in activated carbons modified with phosphoric acid.

This was to also indicate that the samples were also non-graphitized and have high microporous structure (Zhao *et al.*, 2009). Franklin, on the basis of XRD studies, classified activated carbons into two types, based on their graphitizing ability (Franklin, 1951). The non-graphitizing carbons are hard and show a well-developed microporous structure due to the formation of strong cross-linking between the neighbouring randomly oriented elementary crystallites. Whereas, graphitizing carbons have weak cross-linking and had a less developed porous structure (Bansal *et al.*, 1988). Attrition studies were in agreement with the results of nitric modified activated carbons being non-graphitizing carbons as they were found to have high resistance to attrition.

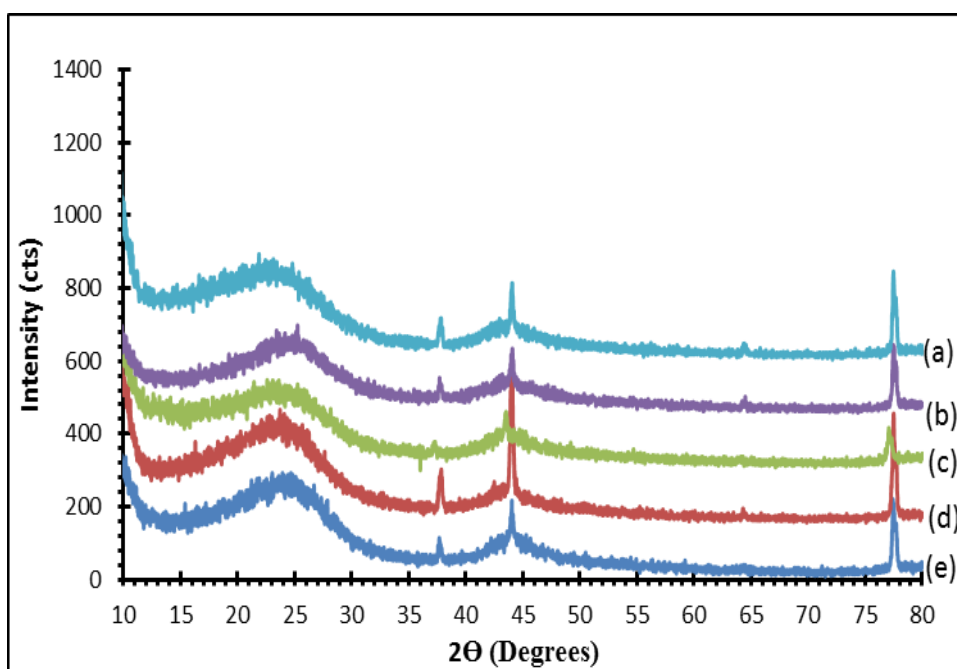
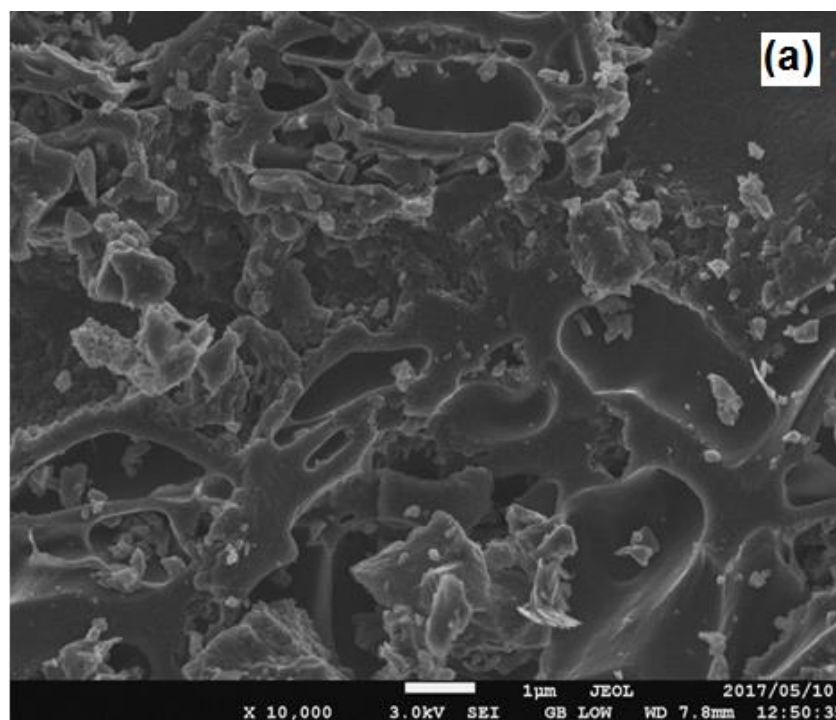


Figure 5.13 XRD patterns of CAC a), MAC b), MACN_{55%} c), MACN_{40%} d) and MACN_{20%} e) adsorbents.

5.2.1.6 SEM analysis of ACs

SEM images of untreated coconut activated carbon, untreated *Macadamia* activated carbons and 55% (v/v) HNO₃ treated *Macadamia* activated carbon are

presented in Figure 5.14. It can be observed that all the adsorbents possessed a rough texture with heterogeneous surface and a variety of randomly distributed pores. These pores are considered as channels to the microporous network. It was also evident from the obtained SEM images that HNO_3 modification was responsible for altering the physical properties and porosity of the materials as there are major differences from the surface morphologies for the untreated *Macadamia* activated carbon and the HNO_3 treated *Macadamia* activated carbon. The surface morphology of the untreated coconut activated carbon was similar to that 55% nitric acid modified activated carbon. The similarity in pore structure for CAC and $\text{MACN}_{55\%}$ could be linked to the BET surface area values obtained which were closer to one another. Therefore, it shows that modification of MAC with 55% concentrated nitric acid yielded a material with similar physical attributes to CAC. Similar results were observed in a study done by Lopes *et al.* (2015) on the modification of pristine *Macadamia* activated carbon with nitric acid.



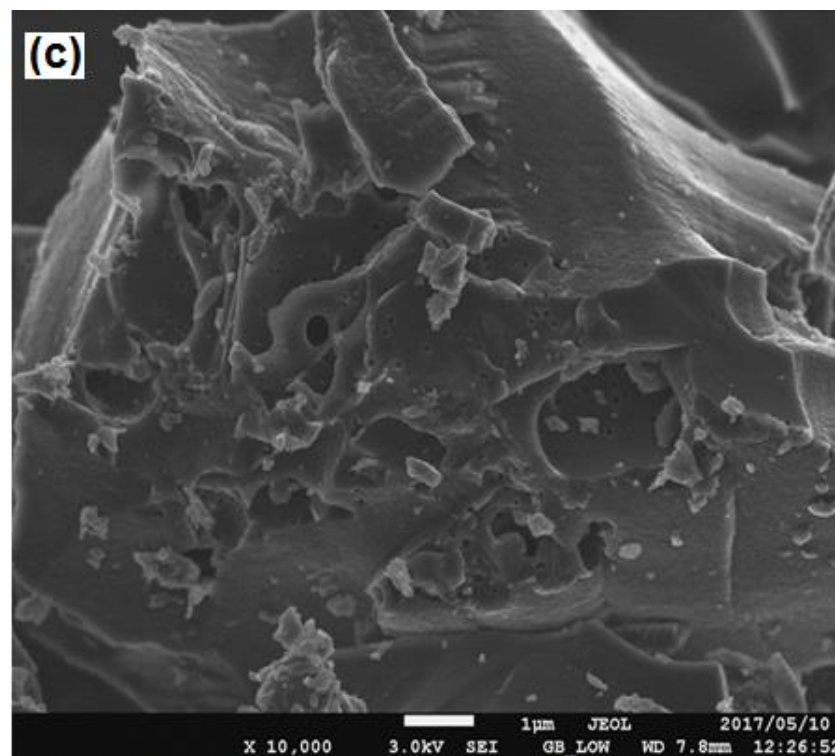
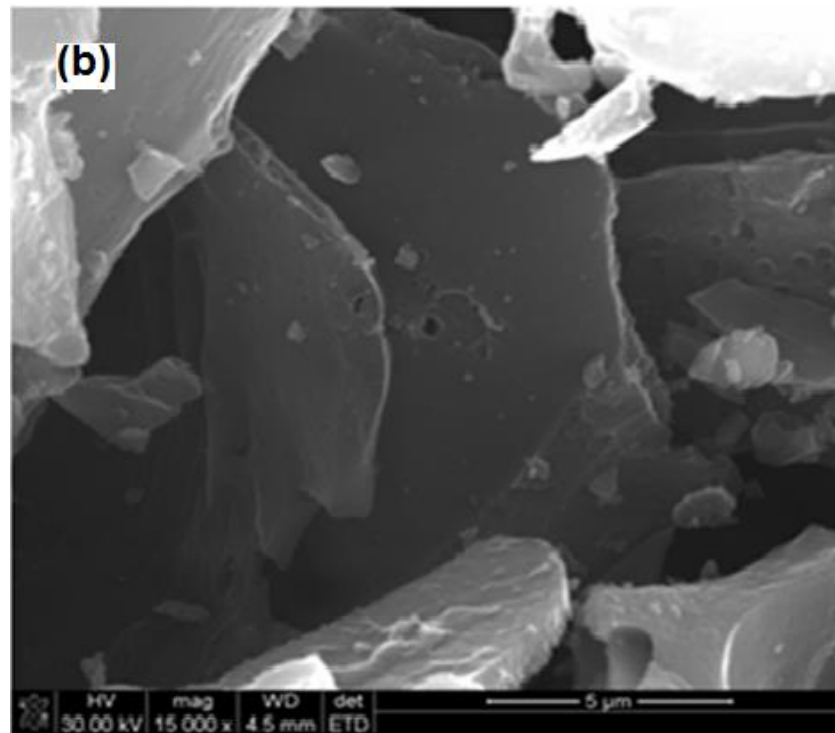


Figure 5.14 SEM images of for CAC (a), MAC (b) and MACN55 % (c).

5.2.2 Physical characterization of activated carbons

Ash content, moisture content, volatile matter, and attrition were determined and the values are displayed in Table 5.9.

5.2.2.1 Ash content

The ash content for CAC, MAC, MACN_{20%}, MACN_{40%} and MACN_{55%} was 4.3, 4.7, 6.2, 6.2 and 8.8 % (Table 5.9). Table 5.9 shows a trend of increasing ash content with increasing concentration of modifying agents (HNO₃). Modification of MAC with nitric acid resulted in a carbon with more inorganic material due to extraction of organic components. That is, high ash content (6.2–8.8%) could be attributed to the residual of entrapped dehydrated acid products (Girgis *et al.*, 2002). Even though the treated AC displayed higher ash content than both CAC and MAC but it was still within the specified limits for mining applications.

Table 5.9 The summary of physical characterization ACs

Type of carbon	Moisture (%)	Ash (%)	Volatile %	Attrition %
Quality specification limits for activated carbon	0-15	0-10	0-40	0-5
CAC	0.4	4.3	4.6	0.25
MAC	0.7	4.7	11.7	0.79
MACN _{20%}	2.1	6.2	12.4	1.14
MACN _{40%}	2.7	6.2	13.6	1.64
MACN _{55%}	2.3	8.8	14.1	1.87

5.2.2.2 Moisture content

The results of the moisture content investigated for the modification of MAC AC with HNO₃ is illustrated on Table 5.9. MACN_{20%} was found to have a moisture content of 2.1% and the highest was 2.3% demonstrated by MACN_{55%} while MAC

reported only 0.7% moisture content. An increase in impregnation ratio of modifying agent HNO_3 was found to increase the moisture content of the activated carbon. Based on the study done by Madhavakrishnan *et al.* (2008), they suggested that no correlation between moisture content and adsorption power of carbon existed. Too much moisture may lead to incorrect solid-liquid ratio dosages for industrial applications. The results showed that HNO_3 modified AC had a higher moisture content compared to the unmodified coconut activated carbon, but was found to still be within the quality specification limits for activated carbon.

5.2.2.3 Volatile matter

The volatile content of quality activated carbons can go up to 40% and it is perceived that the higher the volatile content of the activated carbon, the more it will be resistant to attrition. This was the case with the HNO_3 modified activated carbons as they were found to have a high volatile content of 12.4 % for $\text{MACN}_{20\%}$ 13.65 for $\text{MACN}_{40\%}$ and 14.1% for $\text{MACN}_{55\%}$. MAC was 3.3% and that of CAC was 4.6%. Therefore, an increase in impregnation leads to an increase in volatile matter.

5.2.2.4 Attrition Content

All of the carbon samples used in the research have attrition resistances well below the 2% mark, an indication that the carbons have good attrition resistances. This is particularly true for *Macadamia* carbon, coconut activated carbon samples and the *Macadamia* carbon modified with HNO_3 which had an average percent attrition of 0.25, 0.78 and 1.87% respectively. The carbons make them desirable. The HNO_3 modified AC had a high attrition content compared to the unmodified coconut activated carbon, it is still within the quality specification limits for activated

carbon. Hence the HNO₃ modified AC can still be used as an alternative to the commonly used coconut activated carbon.

5.2.3 Adsorption Studies

5.2.3.1 *Effect of adsorbent dose*

Figure 5.15 shows the results obtained from the optimization of activated carbons sorbent dosage for gold adsorption. It can be observed that the amount of gold adsorbed on activated carbon increased as the adsorbent dosage is increased from 1 to 4 g for all activated carbons investigated.

As the AC dose was increased, free sorption surface and adsorption sites also increased and this lead to an increase in number of available active adsorption sites for the same number of moles of gold species. However, the increase was less than the lower masses, therefore, 4 g was regarded as optimum sorbent dosage even though there was still an increase in the adsorption rate for gold. Thus, in the succeeding studies 4 g of activated carbons were used. The HNO₃ modified AC adsorption rate was similar to the unmodified coconut activated carbon. MAC showed the lowest adsorption rate, followed by MACN_{20%} and MACN_{40%}. MACN_{55%} showed the highest adsorption rate from all the three concentrations studied and was almost overlapping with the CAC displaying similar characteristics in terms of gold adsorption under the same conditions.

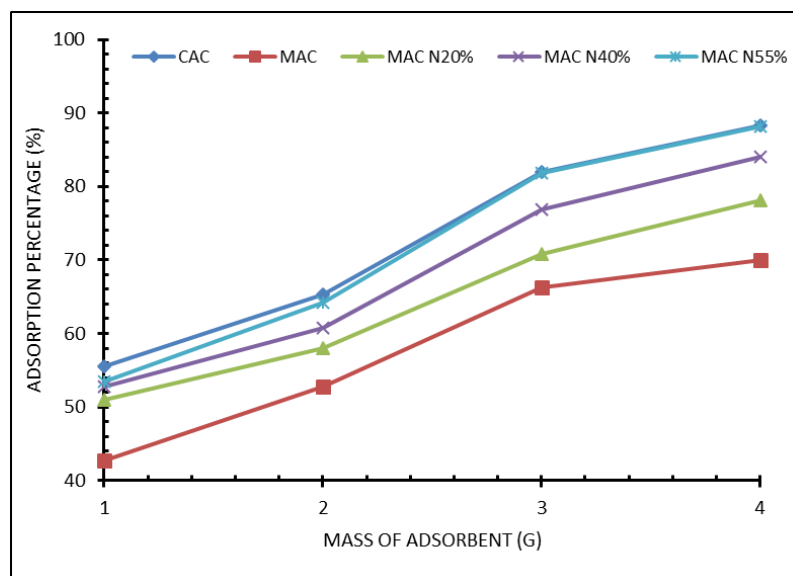


Figure 5.15 Effect of dose of adsorbent on gold adsorbent. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, agitation speed used 150 rpm and initial concentration of solution, 5.622 mg/L.

5.2.3.2 Effect of initial gold concentration

Figure 5.16 shows the results obtained from the optimization of activated carbons for the effect of initial concentration of gold. The percentage removal of gold decreased as the initial gold concentration in the solution was increased from 5.5 to 9.5 mg/L (Figure 5.16a)). This was because at lower concentrations, the ratio of the initial moles of gold species to the available adsorption sites was low and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentration the available adsorption sites for adsorption become fewer compared to the moles of gold species present and hence the percentage removal of gold is dependent on the initial gold concentration. An increase in the initial concentration of gold leads to an increase in the adsorption of gold on activated carbon. This indicated that the initial gold concentration plays an important role in the adsorption of gold on activated carbon. Maximum adsorption was observed at 5.5 mg/L, which was observed for all the carbons. The

adsorption rate ranged from 70% to 90% and the specific adsorption rates were 70%, 78%, 85%, 90% and 91% for MAC, MACN_{20%}, MACN_{40%}, MACN_{55%}, and CAC. Therefore, it shows that MACN_{55%} and CAC had similar adsorption capabilities of gold under the tested conditions. MACN_{55%} can be used as an alternative to the commonly used coconut activated carbon.

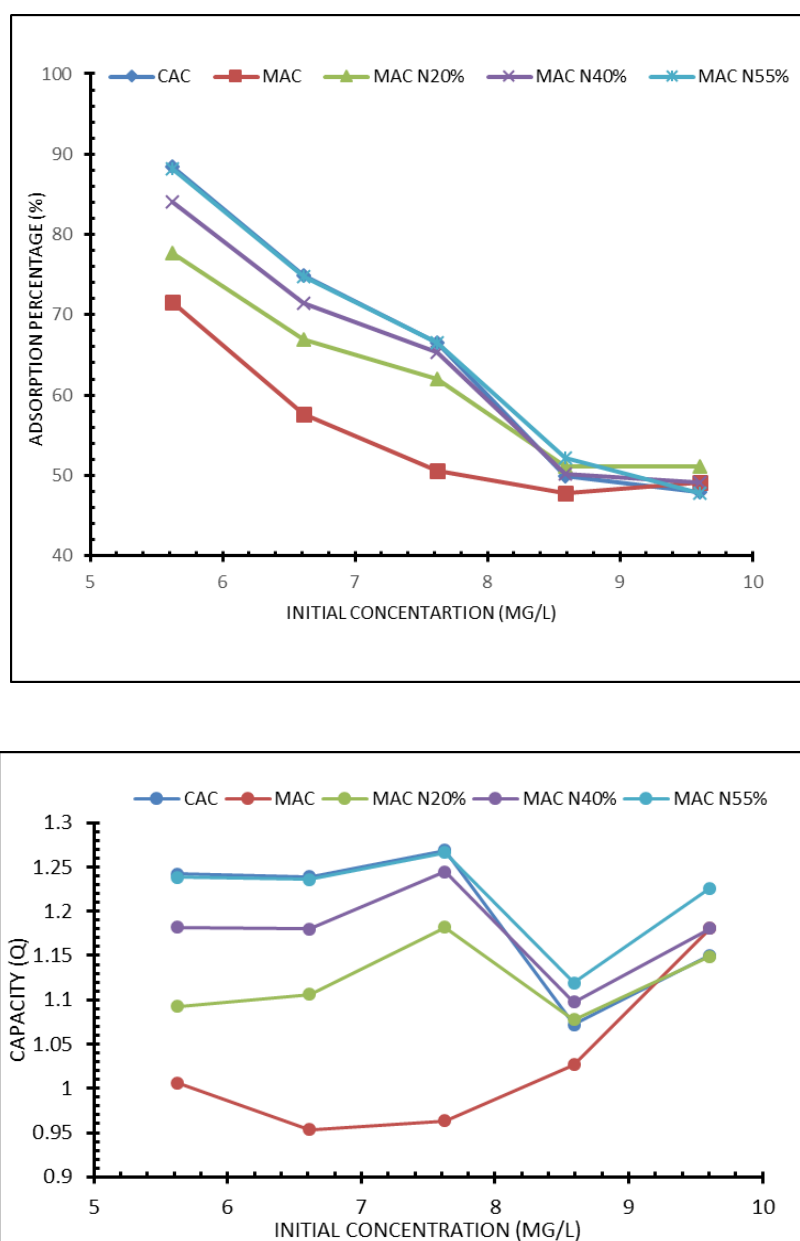


Figure 5.16 Effect of initial concentration on adsorption rate (a) and adsorption capacity (b). (conditions: Solution pH 10; solution volume, 1000 mL; contact time, 1 h, agitation speed used 150 rpm and dosage of carbon, 4 g).

5.2.3.3 Effect of agitation

Figure 5.17 illustrates the effect of shaking speed which was investigated by varying the agitation speed from 50-250 rpm whilst other parameters were kept constant. Adsorption percentage steeply increased from 50-150 rpm then slowed down almost reaching equilibrium between 200-250 rpm. Below 150 rpm it was observed that some of the carbon remained at the base of the bottle implying less contact and at 200-250 rpm the bottles were shaking vigorously leading to spillages. The optimum shaking speed was found to be 200 rpm. However, in the succeeding studies only 150 rpm speed was used to avoid spillages. The observed increase in the percentage of adsorption of gold with shaking speed can be attributed to the improvement in contact between the gold species in solution and the active sites on the carbons, thereby promoting effective transfer of adsorbate ions to the adsorbent site. MACN_{55%} and CAC were overlapping and displaying the highest adsorption percentage compared to other carbons. The order of percentage of adsorption decreased according to the following trend $CAC \approx MACN_{55\%} > MACN_{40\%} > MACN_{20\%} > MAC$. Therefore, functionalization of MAC with nitric acid improved its adsorption percentage for gold ions.

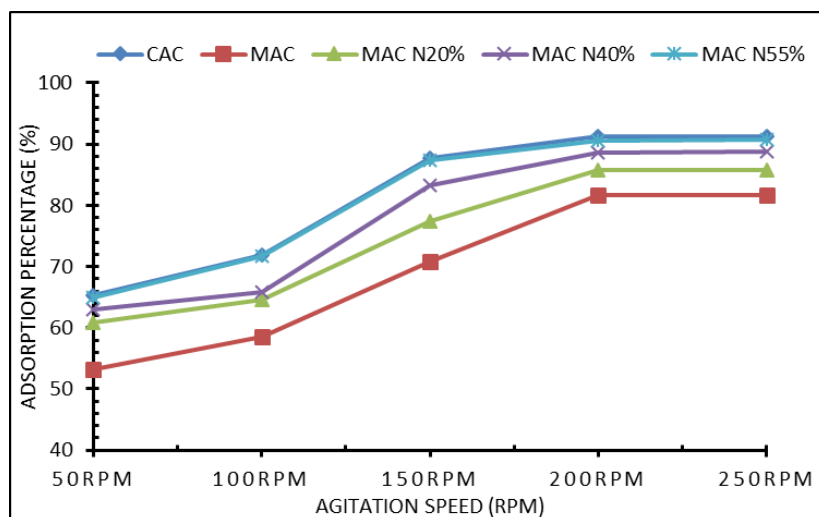


Figure 5.17 Effect of initial agitation speed on gold adsorption. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g and concentration used was 5.7 mg/L.

5.2.3.4 Effect of contact time

The results obtained from varying the time during gold adsorption are displayed in Figure 5.18. The percentage removal of gold ions from solution increased rapidly as the time of agitation was increased from 1 to 5 h, and then slowed down from 5 to 6 h as it attains equilibrium for all the carbons investigated. The observed rapid increase in rate of adsorption initially was because the adsorption sites were more available for the adsorbent-adsorbate interactions, resulting in higher adsorption rate. However, the functional groups started to get saturated as the time increased beyond 5 h resulting in lower adsorption rates and consequently equilibrium. Again, the order of adsorption below 2 h was similar to the study of dosage, concentration and agitation speed effects in that MAC had the lowest adsorption followed by MACN_{20%}, MACN_{40%}, and CAC \approx MACN_{55%}. After 5 h all the carbons seemed to attain similar adsorption capacity and 6 h was regarded as the optimum time.

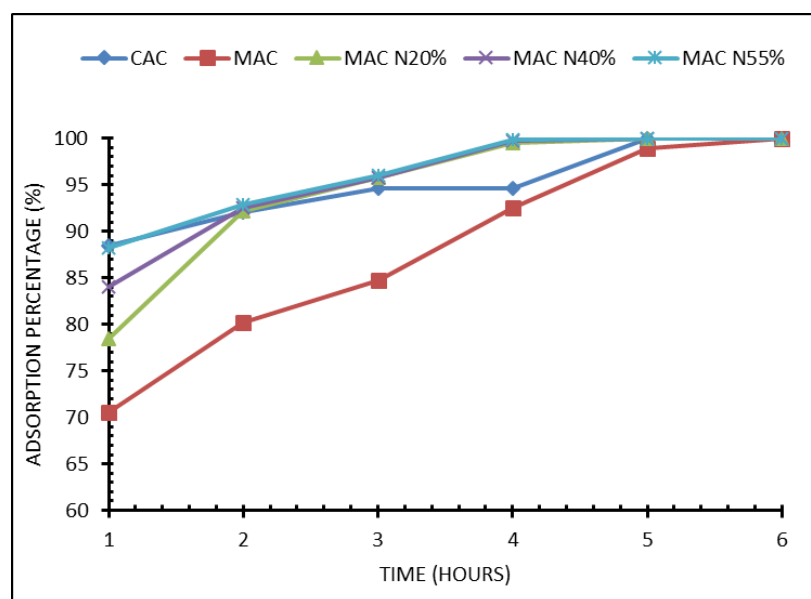


Figure 5.18 Effect of time on gold adsorption. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g, agitation speed used 150 rpm and concentrations used were 5.7 mg/L.

5.2.3.5 Selectivity on adsorption of gold (effect of interfering species)

Selectivity studies was done by selecting metals with similar or less size as the gold ion. These metals included nickel (Ni: Aw 58.69 g mol⁻¹: ionic radius 69 pm), lead (Pb: Aw 65.39 g mol⁻¹: ionic radius 74 pm), iron (Fe: Aw 55.85 g mol⁻¹: ionic radius 64 pm), and copper (Cu: Aw 63.55 g mol⁻¹: ionic radius 72 pm). A mixture containing 4 metal ions in solution together with gold ions of about 6 mg/L solution containing Pb, Ni, Fe Cu and Au was used to investigate the selectivity of the activated carbons. The parameters that were used for the experiment were: time 6 h, pH 10, mass of adsorbent 4 g and 1000 mL for the volume of solution used at agitation speed of 150 rpm. Atomic absorption spectroscopy was used to determine the concentration of the unabsorbed metal ions. The obtained results are illustrated in Table 5.10.

Table 5.10 Effects of competing ions on gold adsorption

Metals absorbed	<i>Adsorption percentage for the activated carbons %</i>				
	CAC	MAC	MACN _{20%}	MACN _{40%}	MACN _{55%}
Copper	3.9	6.6	5.1	5.9	7.2
Iron	4.3	17.2	11.3	9.4	7.9
Nickel	22.5	21.3	16.2	19.4	17.5
Lead	16.5	14.5	14.3	16.5	14.9
Gold	80.8	64.2	69.7	72.5	73.6

The activated carbons were found to have adsorption percentage that was lower than 100% which indicated that the presence of other metals lower the adsorption rate of gold when present in the solution. About 64% adsorption was achieved for MAC, 62% for MACN_{20%}, 72% MACN_{40%}, and 73% for MACN_{55%} and 80% for CAC. The order of selectivity from the examined selective sorption of heavy metals displayed a similar trend to other experiments on adsorption percentage. Amongst the interfering metals that were selected, copper was found to interfere the least and nickel was found to interfere the most for all the activated carbons that were investigated. Similar results were observed from a study done by Sayiner *et al.* (2013) who investigated the effect of silver, nickel and copper cyanides on gold adsorption by activated carbons from leached samples. The observed results were that nickel had a high adsorption rate as compared to the copper which had the lowest adsorption rate.

5.2.3.6 Reusability of HNO_3 activated carbon

It can be observed from the result of the studies that have been done so far that $\text{MACN}_{55\%}$ demonstrated higher adsorption capabilities as compared to other nitric acid modifications. As a result the investigation of reusability of the ACs were carried out using $\text{MACN}_{55\%}$, MAC and CAC for comparison. The results are illustrated in Figure 5.19. A higher than 80% adsorption efficiency was achieved in about 5 cycles for the $\text{MACN}_{55\%}$, which was almost the same as that of CAC. This led to the conclusion that the HNO_3 modified AC can be used as an alternative to the commonly used coconut activated carbon.

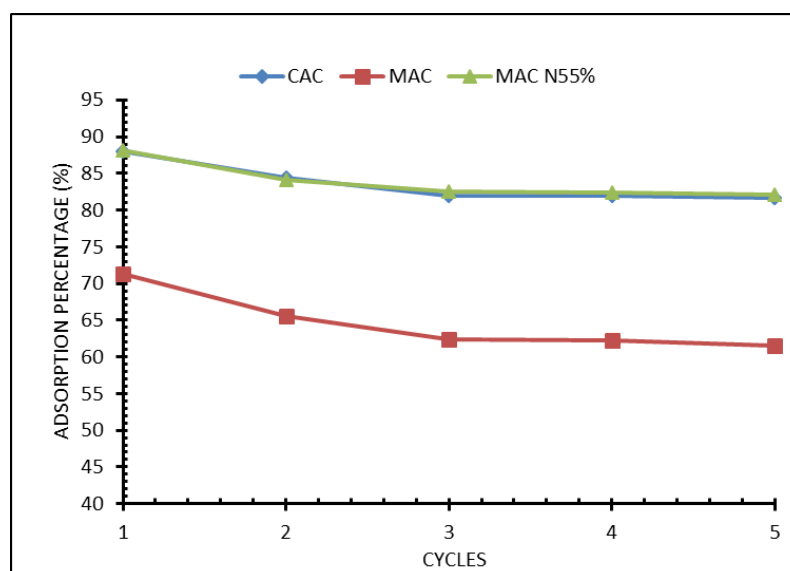


Figure 5.19 shows results for the re-usability of the activated carbons. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g, agitation speed used 150 rpm and concentrations used were 5.7 mg/L.

5.2.3.7 Application of HNO_3 modified activated carbons on real sample

The applicability of the prepared activated carbons for the removal of gold species on real-world samples was carried out using a Barren sample solution from West Wits Chemical Lab. Atomic absorption spectroscopy was used to determine the total metal content of the samples and the results were 5.876 mg/L for Au, 97.800

mg/L for Ni, 4.121 mg/L for Fe, 5.799 mg/L for Cu and 1.113 mg/L for Pb. The pH of the barren sample was measured and adjusted to 10 and the adsorption of gold was carried out in a batch mode. The test parameters were: time 6 h, pH 10, mass of adsorbent 4 g and 1000 mL for the volume of solution used at agitation speed of 150 rpm. Atomic Absorption Spectroscopy was used to determine the concentration of the unabsorbed gold species in real samples. The results are illustrated in Figure 5.20. About 55% adsorption was achieved for MAC and 74% for MACN_{55%} and CAC.

The adsorption percentage removal for the 3 carbons investigated in this study displayed similar results to those which were observed in the study of interfering species. This was due to the fact that real samples (barren solution) contained the same metal species such as Ni, Cu, Pb and Fe which were selected for the study of interfering species. It can be observed that none of the activated carbons reached 100% adsorption percentage from barren samples. This proved that the adsorption rate of gold in the presence of other metals does indeed decrease. The MACN_{55%} proved to have similar adsorption capabilities in all the studies done, this shows that it can be used as an alternative to the CAC that is currently being used in the mining industries.

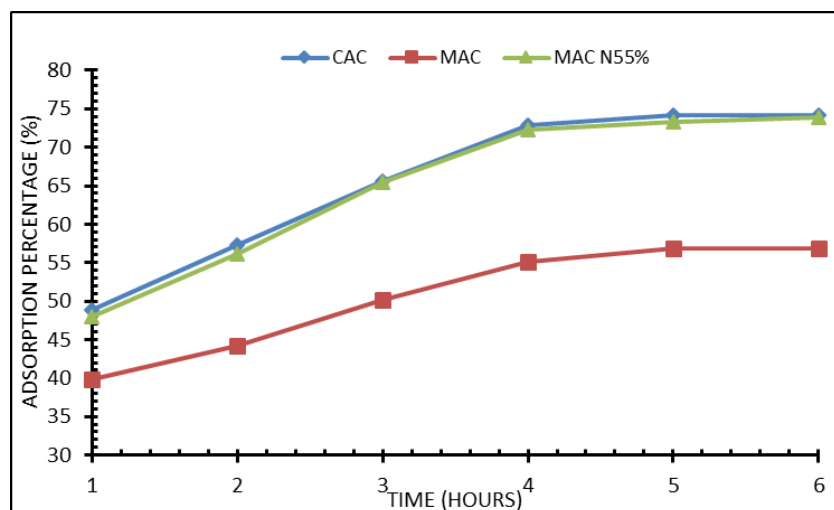


Figure 5.20 shows results for the application on real sample of the activated carbons. Solution pH 10; solution volume, 1000 mL; contact time, 1 h, dosage of carbon, 4 g, agitation speed used 150rpm and the initial concentrations measured were Au=5.876 Ni=97.8, Fe=4.121, Cu=5.799 and Pb=1.113 mg/L.

5.2.3.8 Adsorption isotherms for HNO_3 ACs

The most widely used isotherm for the adsorption of gold onto activated carbon is the Freundlich and the Langmuir isotherm, and the equations were given in section (5.1.3.8). Table 5.11 shows the results of the equilibrium constants for the Freundlich and the Langmuir isotherm fitted to the experimental data. The R^2 values for both Langmuir and Freundlich models were found to fit well to the adsorption data in which the R^2 values were found to be very close to 1. Model parameters k and n were found by a non-linear regression analysis. The observed increase of n values was assigned to a rapid adsorption of Au on activated carbon. Similar results were reported from a study done by Snyders (2015) who observed that direct comparison to gold isotherms found in literature is, however, difficult at best because of the many factors that affect the adsorption of metal cyanide complexes such as the activity of the activated carbon used, the adsorption equipment and stream constituents like pH and cyanide.

Table 5.11 Langmuir and Freundlich isotherms constants for H₃PO₄.

Adsorbents	Langmuir			Freundlich		
	Q _m	b	R ²	K _F	n	R ²
CAC	10.86	102.05	0.94	5.81	5.08	0.96
MAC	3.28	52.11	0.93	4.17	2.54	0.91
MACN _{20%}	5.83	67.38	0.96	5.81	5.08	0.97
MACN _{40%}	8.31	83.73	0.95	5.44	4.06	0.96
MACN _{55%}	10.41	99.34	0.96	5.79	4.9	0.97

5.2.3.8 Kinetic models for HNO₃ ACs

The correlation coefficient values for the pseudo-first and second order kinetics were calculated from the linearized equation 5.3 and 5.4 and the results are given in Table 5.12. From the results, it was observed that correlation coefficient values of the pseudo-second order kinetics produced better quality of linearization compared to those of pseudo-first order kinetics as they were found to be closer to 1. A pseudo-second order further suggested that the type of interaction between Au(CN)₂⁻ and the adsorbent surface of all the activated carbons was chemisorption.

Table 5.12 Kinetic Models constants for HNO₃ ACs

Kinetic Models	Parameters	CAC	MAC	MACN _{20%}	MACN _{40%}	MACN _{55%}
Pseudo-first order	k ₁ (min)	0.0168	0.0158	0.01787	0.01777	0.01684
	q _e (cal)					
	(mg/g)	0.900	1.814	1.057	0.920	0.773
	R ²	0.963	0.907	0.971	0.941	0.948
Pseudo-second order	k ₂					
	(g/mg/min)	0.1026	0.0311	0.07153	0.09175	0.12461
	q _e (cal)					
	(mg/g)	1.429	1.457	1.445	1.436	1.427
	R ²	0.999	0.988	0.998	0.999	0.999

CHAPTER 6: CONCLUSIONS AND FUTURE PERSPECTIVE

6.0 Summary

The focus of this research was to conduct a study in which activated carbons derived from *Macadamia* nut-shells were used in the recovery of gold. These activated carbons have undergone a secondary treatment using different concentrations of HNO_3 and H_3PO_4 to improve their surface adsorption properties. This was done in order to explore if these activated carbons prepared from *Macadamia* shells could be an attractive alternative or a complementary supplement to the coconut shell based carbons that are currently being used in the gold extraction industry. The modification of the commercially prepared *Macadamia* activated carbons was done with 3 different concentrations for both nitric acid and phosphoric acid. Physical characterization was done on the activated carbons by determining attrition, ash content, volatile matter, and moisture content of all the activated carbons. Various techniques which included elemental analysis; Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM) were used for further characterization of the modified *Macadamia* and coconut activated carbons. The adsorption capacity of the activated carbons was investigated. This was done by studying the effect of various parameters such as the effect of initial concentration, time, agitation speed, interfering species and adsorbent dose on the adsorption of gold by the ACs. Further, re-usability studies and subsequent application on real-world samples were also investigated.

6.1. Conclusions

Based on the detailed experimental investigation the conclusions derived are as follows:

- This study demonstrated a successful preparation of phosphoric and nitric modified activated carbons
- The functional groups that were observed from the various nitric and phosphoric modified activated carbons indicated that the aim of increasing the oxygen content on the unmodified *Macadamia* activated carbon was achieved.
- The TGA thermograms showed that the modified *Macadamia* ACs showed a high percentage loss of weight compared to the non-modified AC which attributes to high adsorption properties due to the increase in the pore volume. Generally, the higher the BET surface area and the pore volume, the higher the effectiveness of the activated carbon adsorbing gold ion. Increase in concentration of nitric acid and phosphoric acid produced ACs with higher BET surface areas and pore volume than unmodified ACs.
- The phosphoric acid modified activated carbons were found to have ash content that is higher than the quality specification limits for activated carbon which is between 0-10% whilst the nitric acid modified activated carbons were found to be within limits.
- Both the nitric and phosphoric acid modified activated carbons were found to have moisture content that was within the quality specification limits for activated carbon of 0-15%. This was critical as excess moisture content in the activated carbon leads to an incorrect solid-liquid ratio dosage for industrial applications.

- The volatile content of a quality activated carbons is perceived suitable even if it goes up to 40% but all ACs under study exhibited volatile content well below 40%. The higher volatile content is also related to the ability of ACs to resist attrition.
- All nitric acid modification forms had attrition percentage that was less than 2%. This implied that they were not easily broken and therefore the chances of losing gold through seepage with finer particles of ACS will be minimal. Contrary, phosphoric acid modified activated carbons were found to have high attrition rate which rendered them undesirably for use in the mining industry.
- The MACP_{60%} was found to be the most effective from the three concentrations investigated for the phosphoric acid modified activated carbons in all the adsorption studies yet proved to have lower adsorption capabilities compared to those of CAC.
- The MACN_{55%} was found to be the most effective from the three modification of nitric acid and was found to have similar adsorption capabilities with those of CAC in all adsorption studies.

6.2 General conclusion

From the various conclusions brought forward in the preceding section, it is clear that the phosphoric modified activated carbons cannot be used as an alternative to the current CAC being used in the mining industry. However, the MACN_{55%} proved that it can be attractive alternative or a complementary supplement to the coconut shell based carbons that are currently being used in the gold extraction industry.

6.3 Recommendations

- The future work emanating from this study, include the production of ACs with even better surface characteristics through different routes such as physical

activation, two stage activation and microwave heating etc which can be compared with the results obtained with chemical activation.

- Saving costs mainly depends on the selection of raw material and method of preparation of AC. Thus, the cost estimation should be carried out to evaluate the potential application of the adsorbent in actual practice.
- Detailed research on desorption of gold and regeneration of AC is essential to evaluate the efficiency of the process which needs an immediate attention.
- Carbon in pulp studies should be carried out to test the suitability of prepared nitric modified AC as adsorbent in metallurgical plants for gold recovery.
- Further modifications of ACs, with organic ligands to improve the selectivity of gold abstraction since gold is likely to be present in ore with other base metals just as Ni, Pb, Fe, and Cu.

7. References

ABDULQADIR, J.N R., Preparation and characterization of modified activated charcoal based on *Ferula Communis* and its adsorptive behaviour, masters, Thesis, Eastern Mediterranean University Gazimağusa, North Cyprus (2014).

ACHARYA, J., SAHU, J.N., SAHOO, B.K., MOHANTY, C.R., MEIKAP, B.C, 2001, 'Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride' *Chemical Engineering Journal*, 150 (1): 25-39.

ADINATA, D., DAUD, W.M.A.W., AROUA, M.K., 2007, 'Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 ' *Bioresource Technology*, 98: 145-149.

AHMADPOUR, A., DO, D., 1997 'The preparation of activated carbon from *Macadamia* nutshell by chemical activation' *Carbon*, 35: 1723-1732.

ANTAL, M. J., GRONLI, M., 2003, 'The art, science, and technology of charcoal production' *Industrial and Engineering Chemistry Research*, 42: 1619-1640.

ANSARI, K. R., OMIDVARI, R., 2005, 'Adsorption of mercuric ion from aqueous solutions using activated carbon' *Polish Journal of Environmental Studies* 14: 185-188.

AWORN, A., THIRAVETYAN, P., NAKBANPOTE, W., 2009, 'Preparation of CO_2 activated carbon from corncob for methylene glycol adsorption', *Colloids and Surfaces' Physicochemical Engineering Aspects*, 333:19-25.

BAÇAOU, A., YAACOU, A., DAHBI, A., BENNOUNA, C., PHAN TAN LUU, R., MALDONADO-HODAR, F. J., RIVERA-UTRILLA, J., MORENO-CASTILLA, C., 2001, 'Optimization of conditions for the preparation of activated carbons from olive-waste cakes' *Carbon*, 39: 425-432.

BABEL, S., KURNIAWAN, T.A., 2004, 'Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan' *Chemosphere*, 54 (7): 951-967.

BALCI, S., DOGU, T. and YUCEL, H., 1994, 'Characterization of activated carbon produced from almond shell and hazelnut shell' *Journal of Chemical Technology and Biotechnology* 60: 419-426.

BANSAL, R. C., GOYAL, M., 2005, 'Activated carbon adsorption' Taylor and Francis Group, Florida.

BANSODE, R.R., LOSSO, J.N., MARSHALL, W.E., RAO, R.M., PORTIER, R.J., 2003, 'Adsorption of volatile organic compounds by pecan shell and almond shell based granular activated carbons' *Bioresource Technology*, 90: 175-184.

BASTA, A.H., FIERRO, V., EL-SAIED, H., CELZARD, A., 2009 '2-steps KOH activation of rice straw: An efficient method for preparing high-performance activated carbons' *Bioresource Technology*, 100: 3941-3947.

BENTANCUR, M., MARTINEZ, J.D., MURILLO, R., 2009 'Production of activated carbon by waste tire thermochemical degradation with CO₂' *Journal of Hazardous Materials*, 168: 882-887.

BUDINOVA, T., EKINCI, E., YARDIM, F., GRIMM, A., BJORNBOM, E., MINKOVA, V., GORANOVA, M., 2006, 'Characterization and application of activated carbon produced by H₃PO₄ and water vapor activation' *Fuel Process Technology*, 87: 899-905.

CASTRO-MUNIZ, A., SUAREZ-GARCIA, F., MARTINEZ-ALONSO, A., TASCÓN, J.M.D., 2011, 'Activated carbon fibers with a high content of surface functional groups by phosphoric acid activation of PPTA' *Journal of Colloid and Interface Science*, 361: 307-315.

- CATURLA, F., MOLINA-SABIO, M., RODRÍGUEZ-REINOSO, F., 1991
'Preparation of Activated carbon by chemical activation with ZnCl_2 ' *Carbon*, 29:
999-1007.
- CERMINARA, P.J., SORIAL, G.A., PAPADIMAS, S.P., SUIDAN, M.T.,
MOTELB, M.A., SPETH, T.F., 1995, 'Effect of influent oxygen concentration
on the GAC adsorption of VOCs in the presence of BOM' *Water Research*, 29 (2):
409-419.
- COOK, D., NEWCOMBE, G., SZTAJNBOK, P., 2001, 'The application of
powdered activated carbon for miband geosmin removal: predicting pac doses in
four raw waters' *Water Research*, 35 (5): 1325-1333.
- CRONJE, K.J., CHETTY, K., CARSKY, M., SAHU, J.N., MEIKAP, B.C., 2011,
'Optimization of chromium(VI) sorption potential using developed activated
carbon from sugarcane bagasse with chemical activation by zinc chloride'
Desalination, 275: 276-284.
- DAS, G. K., ACHARYA, S., DAS, R. P., 1996, 'Jarosite: A Review' *Mineral
Processing Extractive Metallurgy*, 16: 185-210.
- DAVIDSON, R. J., 1974, 'The mechanism of gold adsorption in activated
charcoal' *Journal of South Africa Institution in Mining Metallurgy* 75: 67-76.
- DAVIDSON, R. J., VERONESE, V., NKOSI, M. V., 1979, 'The use of activated
carbon for the recovery of gold and silver from gold-plant solutions' *Journal of
South Africa Institution in Mining Metallurgy* 230: 281-297.
- DEJANG, N., SOMPRASIT, O., CHINDARUKSA, S., 2015, 'A preparation of
activated carbon from Macadamia shell by microwave irradiation activation.

DENG, H., ZHANG, G., XU, X., TAO, G., DAI, J, 2010, 'Optimization of preparation of activated carbon from cotton stalk by microwave assisted phosphoric acid – chemical activation' *Journal of Hazardous Materials*, 182: 217-224.

Department of Agriculture, Forestry and Fisheries (DAFF), 2012. A profile of the South African *Macadamia* nuts market value chain. Arcadia.

DERBYSHIRE, F., ANDREWS, R., JAQUES, D., JAGTOYEN, M., KIMBER, G., RANTELL, T., 2001, 'Synthesis of isotropic carbon fibers and activated carbon fibers from pitch precursors' *Fuel*, 80 (3): 345-356.

DIAO, Y., WALAWENDER, W.P., FAN, L.T., 2002, 'Activated carbons prepared from phosphoric acid activation of grain sorghum' *Bioresource Technology*, 81: 45-52.

DIAZ-DIEZ, M.A., GOMEZ-SERRANO, V., FERNANDEZ, D., GONZALEZ, C., CUERDA-CORREA, E.M., and MACIAS-GARCIA, A., 2004, 'Porous texture of activated carbons prepared by phosphoric acid activation of woods' *Applied Surface Science* 238: 309-313.

DREISINGER, D., MOLLEMAN, E, 2002, "The treatment of copper–gold ores by ammonium thiosulfate leaching' *Hydrometallurgy*, 66: 1–21.

DUBININ, M.M., 1966, 'Porous structure and adsorption properties of active carbons', Chemistry and Physics of Carbon, vol. 2. *Marcel Dekker, New York*.

DUMAN, O., AYRANCI, E., 2010, 'Attachment of benzo-crown ethers onto activated carbon cloth to enhance the removal of chromium, cobalt and nickel ions

from aqueous solutions by adsorption' *Journal of Hazardous Materials*, 176 (1-3): 231-238.

EL-HENDAWY, A.A., ALEXANDER, A.J., ANDREWS, R.J., FORREST, G., 2008 'Effects of activation schemes on porous, surface and thermal properties of activated carbons prepared from cotton stalks' *Journal of Analytical and Applied Pyrolysis*, 82: 272-278.

EUGENE W., MUJUMDAR, A. S., 2009, 'Gold Extraction and Recovery Processes' *Minerals, Metals and Materials Technology Centre (M3TC) National University of Singapore*. Singapore.

FIERRO, V., MUNIZ, G., BASTA, A.H., EL-SAIED, H., CELZARD, A., 2010, 'Rice straw as precursor of activated carbons: Activation with ortho-phosphoric acid' *Journal of Hazardous Materials*, 181: 27-34.

FONG LO, S., WANG, S. W., TSAI, M., LIN, L., 2012, 'Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons' *Chemical Engineering Research and Design*, 90 (9): 1397-1406.

FOO, K.Y., HAMEED, B.H., 2011, 'Porous structure and adsorptive properties of pineapple peel based activated carbons prepared via microwave assisted KOH and K₂CO₃ activation' *Microporous and Mesoporous Materials*, 148: 191-195.

FRASER, K. S., WELLS, J. A., 1991, 'Processing of refractory gold ores' *Minerals Engineering*, 4: 1029-1041.

GANAN, J., GONZALEZ, J.F., GONZALEZ -GARCIA, C.M., RAMIRO, A., SABIO, E., ROMAN, S., 2006, 'Air activated carbons from almond tree pruning: Preparation and characterization' *Applied Surface Science*, 252: 5988-5992.

POINERN, G.E.J., SENANAYAKE, G., SHAH, N., THI-LE, X.N., PARKINSON, G.M., DEREK FAWCETT, D., 2011, 'Adsorption of the aurocyanide, complex on granular activated carbons derived from *Macadamia* nut shells' *Mining Engineering* 24: 1694–1702

GIRGIS, B.S., EL-HENDAWY, A.N.A., 2002, 'Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid' *Microporous and Mesoporous Materials*, 52: 105-117.

GOMEZ-SARRANO, V., CUERDA-CORREA, E.M., FERNANDEZ-GONZALEZ, M.C., ALEXANDRE-FRANCO, M.F., MACIAS-GARCIA, A., 2005, 'Preparation of activated carbons from chestnut wood by phosphoric acid chemical activation. Study of microporosity and fractal dimension' *Materials Letters*, 59: 846-853.

GOTTIPATI, R., 2013 Preparation and characterization of microporous activated carbon from biomass and its application in the removal of chromium (VI) from aqueous phase, Ph.D. Thesis, National Institute of Technology Rourkela, Odisha.

GREGG S.J., SINGG K.S.W, 1982, 'Adsorption, surface area, and porosity' *Carbon*, 86: 957.

GUO, Y., ROCKSTRAW, D.A., 2007, 'Activated carbons prepared from rice hull by one-step phosphoric acid activation' *Microporous and Mesoporous Materials*, 100: 12-19.

- HAI, F.I., YAMAMOTO, K., NAKAJIMA, F., FUKUSHI, K., 2011
'Bioaugmented membrane bioreactor (MBR) with a GAC – packed zone for high rate textile wastewater treatment' *Water Research*, 45 (6): 2199-2206.
- HAIMOUR, N. M., EMEISH, S. ,2005, 'Utilization of date stones for production of activated carbon using phosphoric acid' *Waste Management*, 26: 651-660.
- HAYASHI, J., HORIKAWA, T., TAKEDA, I., MUROYAMA, K., ANI, F.N., 2002, 'Preparing activated carbon from various nutshells by chemical activation with K_2CO_3 ' *Carbon*, 40: 2381-2386.
- HAYKIRI-ACMA, H., 2006, 'The role of particle size in the non-isothermal pyrolysis of hazelnut shell' *Journal of Analytical and Applied Pyrolysis*, 75: 211-216.
- HAO, G.P., LI, W.C., WANG, S., WANG, G.H., QI, L., LU, A.H., 2011, 'Lysine-assisted rapid synthesis of crack free hierarchical carbon monoliths with a hexagonal array of mesopores' *Carbon*, 49: 3762-3772.
- HARRIS, S. LIU, Z., 2008, 'Imagine the atomic structure of activated carbon' *Journal of Physics: Condensed Matter*, No.20:1-5.
- HIJNEN, W.A.M., SUYLEN, G.M.H., BAHLMAN, J.A., BROUWER-HANZENS, A., MEDEMA, G.J., 2010, 'GAC adsorption filters as barriers for viruses, bacteria and protozoan (oo) cysts in water treatment. *Water Research*' 44 (4): 1224-1234.

HORIKAWA, T., KITAKAZE, Y., SEKIDA, T., HAYASHI, J., M., 2010
'Characteristics and humidity control capacity of activated carbon from bamboo'
Bioresource Technology, 101: 3964-3969.

HUANG Y. CANDELARIA L.S, LI Y, LI Z, TIAN J, ZHANG L, CAO G .,2014
'Sulfurized activated carbon for high energy density supercapacitors' *Journal of Power Sources* 252: 90-97

HUNG, J.J., The production of activated carbon from coconut shells using
pyrolysis and fluidized bed reactors. Honors degree Report, University of Arizona
(2012) .

HYLANDER, L. D., 2007, 'Comparison of different gold recovery methods with
regard to pollution control and efficiency' *Journal of Environmental Sciences* 35
(1): 52–56.

JIA, Y. 2000, Adsorption of heavy metal ion species from aqueous solution on
activated carbon. PhD Thesis, University of Newcastle-upon-Tyne.

KAWANO, T., KUBOTA, M., ONYANGO, M.S., WATANABE, F.,
MATSUDA, H., 2008, 'Preparation of activated carbon from petroleum coke by
KOH chemical activation for adsorption heat pump' *Applied Thermal Engineering*,
28: 865-871.

KENNEDY, L.J., VIJAYA, J.J., KAYALVIZHI, K., SEKARAN, G., 2007,
'Adsorption of phenol from aqueous solutions using mesoporous carbon prepared
by two-stage process' *Chemical Engineering Journal*, 132: 279-287.

- KILIC, M., APAYDIN-VAROL, E., PUTUN, A. E., 2012, 'Preparation and surface characterization of activated carbons from euphorbia rigida by chemical activation with $ZnCl_2$, K_2CO_3 , NaOH And H_3PO_4 ' *Applied Surface Science*, 261: 247-254.
- KHAMBHAT, Y., MODY, K., BASHA, S., 2012, 'Efficient removal of Brilliant Blue G (BBG) from aqueous solutions by marine aspergillus wentii: kinetics, equilibrium and process design' *Ecological Engineering* Vol.41: 74-83.
- KLIJANIENKO, A., LORENC-GRABOWSKA, E., GRYGLEWICZ, G., 2008, 'Development of mesoporosity during phosphoric acid activation of wood in steam atmosphere' *Bioresource Technology*, 99 (15): 7208-7214.
- KO, Y.N., CHOI, U.S., KIM, J.S., PARK, Y.S., 2002, 'Novel synthesis and characterization of activated carbon fiber and dye adsorption modeling' *Carbon*, 40 (14): 2661-2672.
- KONDOS, P.D, DESCHENES, G., MORRISON, R.M., 1995 *Hydrometallurgy* 39, 235.
- KONG, J., YUE, Q., HUANG, L., GAO, Y., SUN, Y., GAO, B. LI, Q., WANG, Y., 2013, 'Preparation, characterization and evaluation of adsorptive properties of leather waste based activated carbon via physical and chemical activation' *Chemical Engineering Journal*, 21: 62–71.
- LAZARO , M.J., GALVEZ, M.E., ARTAL, S., PALACIOS, J.M., MOLINER, R., 2007 'Preparation of steam-activated carbons as catalyst supports' *Journal of Analytical and Applied Pyrolysis*, 78 (2): 301-315.

LEI, S., MIYAMOTO, J., KANO, H., NAKAHIGASHI, Y., KANEKO, K., 2006, 'Enhancement of the methylene blue adsorption rate for ultra-microporous carbon by addition of mesopores' *Carbon*, 44 (10): 1884-1890.

LIU, T.H., 2010, 'Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation' *Chemical Engineering Journal*, 158: 129-142.

LIU, C., LIANG, X., LIU, X., WANG, Q., TENG, N., ZHAN, L., ZHANG, R., QIAO, W., LING, L., 2008, 'Wettability modification of pitch-based spherical activated carbon by air oxidation and its effects on phenol adsorption' *Applied Surface Science*, 254: 2659-2665.

LOPES, A.S.C, CARVALHO, S.M.L, BRASIL, D.S.B., MENDES, R.A, LIMA M.O, 2015, 'Surface modification of commercial activated carbon for the treatment of benzene and Toulene' *Analytical Chemistry Journal*, 6: 528-538.

LU, Z., MAROTO-VALER, M., SCHOBERT, H.H., 2010, 'Catalytic effects of inorganic compounds on the development of surface areas of fly ash carbon during steam activation' *Fuel*, 89: 3436-3441.

LUA, A.C., YANG, T., 2005, 'Characteristics of activated carbon prepared from pistachio-nut shell by zinc chloride activation under nitrogen and vacuum conditions' *Journal of Colloid and Interface Science*, 290: 505-513.

MAMCILOVIC, M., PURENOVIC, M., BOJIC, A., ZARUBICA, A., RANDELOVIC, M., 2011, 'Removal of lead (II) ions from aqueous solutions by adsorption onto pine cone activated carbon' *Desalination*, 276 (1-3): 53-59.

MARSDEN, J. O., HOUSE, C. L., 2006, “The Chemistry of Gold Extraction”, 2nd Ed, Ellis Horwood, *New York, NY*.

MARSH, H., RODRIGUEZ-REINOSO, F., 2006. ‘Activated carbon’ 1st Edition, *Elsevier*, Kidlington.

MENENDEZ-DIAZ, J.A., MARTIN-GULLON, I., 2006, ‘Types of carbon adsorbents and their production’ *Interface Science and Technology*, 7: 1-47.

McCRAKEN, D., 1993, Gold mining in the nineteen nineties: The complete book of modern gold mining procedure. *New Era Publications*.

MOHAMAD-NOR, N., LAU, L. C., LEE, K. T., MOHAMED, A., 2013, ‘Synthesis of activated carbon from lignocellulosic biomass and its applications in air pollution control—a review’ *Journal of Environmental Chemical Engineering*, 1 (4): 658–666.

MOGALE, M, 2012 ‘A value of the South African Macadamia nuts market value chain’, viewed on 03 May 2015 from www.samac.org.za.

MONSER, L., ADHOUM, N., 2002, ‘Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater’ *Separation and Purification Technology*, 26: 137-146.

MOPOUNG, S., AMORNSAKCHAI, P., SOMROOP, S., 2016 ‘Characterization of phosphoric acid modified activated carbon fiber from fiber waste of pineapple leaf fiber production processing’ *Carbon Science Technology* 8(1): 1-12.

NABAIS, V., LAGINHAS, C., CARROTT, R., CARROTT, M., AMOROS, C., 2013, ‘Surface and porous characterization of activated carbons made from a novel biomass precursor, the esparto grass’ *Applied Surface Science*, 265: 919-924.

NABAIS, J.V., CARROTT, P., CARROTT, M.M.L.R., LUZ, V., ORTIZ, A.L., 2008, 'Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor: The coffee endocarp' *Bioresource Technology*, 99: 7224-7231.

NABAIS, J.V., NUNES, P., CARROTT, P., CARROTT, M.M.L.R., GARCIA, A.M., DIAZ-DIAZ, M.A., 2008, 'Production of activated carbons from coffee endocarp by CO₂ and steam activation' *Fuel Processing Technology*, 89: 262-268.

NAMASIVAYAM, C., SANGEETHA D., GUNASEKARAN, R., 2007, 'Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from Jatropha husk, an agroindustrial solid waste' *Process Safety and Environmental Protection*, 85 (2): 181-184.

NAHIL, M.A., WILLIAMS, P.T., 2011, 'Recycling of carbon fiber reinforced polymeric waste for the production of activated carbon fibers' *Journal of Analytical and Applied Pyrolysis*, 91 (1): 67-75.

NICOL, M.J., FLEMING, C.A., CROMBERGE, G., 1984. 'The adsorption of gold cyanide onto activated carbon. 2. Application of the kinetic model to multistage adsorption circuits' *Journal of South Africa Institute of Mineral Metallurgy* 84: 50–54.

OLORUNDARE, O. F., KRAUSE, R. W., OKONKWO, J. O., MAMBAPONTENTIAL, B. B., 2012, 'Application of activated carbon from maize tassel for the removal of heavy metals in water' *Physics and Chemistry of the Earth, Parts A/B/C*: 104-110.

ORMAD, M.P., MIGUEL, N., CLAVER, A., MATESANZ, J.M., OVELLEIRO, J.L. 'Pesticides removal in the process of drinking water production' *Chemosphere*, 71 (1): 97-106.

OULD-DRISS, A., STITOU, M., CUERDA-CORREA, E.M., FERNANDEZ-GONZALEZ, C., MARCIAS-GARCIA, A., ALEXANDRE-FRANCO, M.F., GOMEZ-SERRANO, V., 2011, 'Preparation of activated carbons from olive-tree wood revisited. II. Physical activation with air' *Fuel Processing Technology*, 92: 266-270.

PEZOTI, O.J, CAZETTAA, L.A, GOMESA, R.C, BARIZAOA, E.O, SOUZAA, I.P.A.F., MARTINSAA, C., ASEFAB, T., ALMEIDAAV, C., 2014, 'Synthesis of ZnCl₂-activated carbon from *Macadamia* nut endocarp (*Macadamia integrifolia*) by microwave-assisted pyrolysis: Optimization using RSM and methylene blue adsorption' *Journal of Analytical and Applied Pyrolysis* 105 :166–176.

QIAN, Q., MACHIDA, M., TATSUMOTO, H., 2007, 'Preparation of activated carbons from cattle-manure compost by zinc chloride activation' *Bioresource Technology*, 98: 353-360.

ROMEO, A., CARLOS H., 1993, 'A comparison of adsorption characteristics of various activated carbon' *Journal of Chemical Technology Biotechnology* 56: 77-82.

ROSAS, J.M., BEDIA, J., RODRIGUEZ-MIRASOL, J., CORDERO, T., 2009 'HEMP – derived activated carbon fibers by chemical activation with phosphoric acid' *Fuel*, 88:19-26.

SAHU, J.N., ACHARYA, J., MEIKAP, B.C., 2010, 'Optimization of production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology' *Bioresource Technology*, 101:1974-1982.

SALVADOR, F., SANCHEZ-MONTERO, M.J., MONTERO, J., IZQUIERDO, C., 2009, 'Hydrogen storage in carbon fibers activated with supercritical CO₂: Models and the importance of porosity' *Journal of Power Sources*, 190: 331-335.

SAN-MIGUEL, G., FOWLER, G. D. SOLLARS, C. J., 2003, 'A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber' *Carbon*, 41: 1009-1016.

SATYAWALI, Y., BALAKRISHNAN, M., 2009, 'Performance enhancement with powdered activated carbon (PAC) addition in a membrane bioreactor (MBR) treating distillery effluent' *Journal of Hazardous Materials*, 170 (1): 457-465.

SCHARF, R.G., JOHNSTON, R.W., SEMMENS, M.J., HOZALSKI, R.M., 2010 'Comparison of batch sorption tests, pilot studies, and modeling for estimating GAC bed life' *Water Research*, 44 (3): 769-780.

SCHIER DE LIMA, L., QUINAIA S.P, MELQUIADES, F.L, GABRIEL E.V.,2014, 'Characterization of activated carbons from different sources and the simultaneous adsorption of Cu, Cr, and Zn from metallurgic effluent' *Separation and Purification Technology* 122: 421–430.

SHARIFAN, S., A comparative optimisation study of activated carbon production from hazelnut shells by thermal and microwave heating methods Ph.D. Thesis, Imperial College London 2013.

SHEN, Z., MA, J., MEI, Z., ZHANG, J., 2010, 'Metal chlorides loaded on activated carbon to capture elemental mercury' *Journal of Environmental Sciences*, 22 (11: 1814-1819.

SILGADO, K., MARRUGO, G., PUELLO, J., 2014. 'Adsorption of chromium(VI) by activated carbon produced from oil palm endocarp' *Chemical Engineering Transactions*, 37, 721-726.

SITTHIKHANKAEWA, R., SOMRUDEE, P., RANTANAWAN, K., SUDHIBHUMI P., SUTTICHA, A. NAVADOL, L., 2011, 'Comparative study of hydrogen sulfide adsorption by using alkaline impregnated activated carbons for Hot Fuel Gas Purification' *Energy Procedia* 9:15 – 24

SOLEIMANI, M., Gold adsorption from dilute solutions with carbon adsorbents and modeling of the adsorption system, Ph.D. Thesis, Amirkabir University of Technology, Tehran (2007)

SRINIVASAKANNAN, C. and ZAILANI ABU BAKAR, M., 2004, 'Production of activated carbon from rubber wood sawdust' *Biomass and Bioenergy*, 27:89-96.

STREZOV, V., PATTERSON, M., ZYMLA, V., FISHER, K., EVANS, T. J., NELSON, P. F., 2007, 'Fundamental aspects of biomass carbonization' *Journal of Analytical and Applied Pyrolysis*, 79: 91-100.

SUFNARSKI, M.B.S., 1999, 'The regeneration of granular activated carbon using hydrothermal technology' Master of Science in Engineering, University of Texas, Austin.

SUHAS, CARROTT, P. J. M. RIBEIRO CARROTT, M. M. L., 2007, 'Lignin – from natural adsorbent to activated carbon: A review' *Bioresource Technology*, 98: 2301-2312.

TAN, I. A. W., AHMAD, A. L. and HAMEED, B. H., 2007, 'Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology' *Chemical Engineering Journal*, 137: 462-470.

TAY, T., UCAR, S. KARAGÖZ, S., 2009, 'Preparation and characterization of activated carbon from waste biomass' *Journal of Hazardous Materials*, 165: 481-485.

TOLES, C. A., MARSHALL, W. E. JOHNS, M. M., 1997, 'Granular activated carbons from nutshells for the uptake of metals and organic compounds' *Carbon*, 35 (9): 1407-1414.

TSENG, R.L., TSENG, S.K., WU, F.C., HU, C.C., WANG, C.C., 2008, 'Effects of micropore development on the physicochemical properties of KOH-activated carbons' *Journal of Chinese Institute of Chemical Engineers*, 39: 37-47.

VALDES, H., SANCHEZ, M., RIVERA, J., 2002, 'Effect of ozone treatment on surface properties of activated carbon' *Langmuir*, 18: 2111-2116.

VALIX, M., CHEUNG, W.H., ZHANG, K., 2006, 'Role of heteroatoms in activated carbon for removal of hexavalent chromium from wastewaters' *Journal of Hazardous Materials B*, 135: 395- 405.

VAN DEN BERG, R., 2000. 'Inhibition of the pregrobbing phenomenon in gold ores' Masters dissertation. Cape Technicon.

VASU, A.E, 2008, 'Surface Modification of activated carbon for enhancement of nickel(II) adsorption' *Journal of Chemistry*, 5 (4): 814-819.

WANG, J., ZHAO, F., HU, Y., ZHAO, R., LIU, R., 2009, 'Modification of activated carbon fiber by loading metals and their performance on SO₂ removal' *Chinese Journal of Chemical Engineering*, 14(4): 478-485.

WANG, X., LIANG, X., WANG, Y., WANG, X., LIU, M., YIN, D., XIA, S., ZHAO, J., ZHANG, Y., 2011, 'Adsorption of copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation' *Desalination*, 278 (1-3): 231-237.

WILLIAMS, T. P., REED, R. A., 2004, 'High grade activated carbon matting derived from the chemical activation and pyrolysis of natural fibre textile waste' *Journal of Analytical and Applied Pyrolysis* 71(2): 971-986.

WU, F.C., WU, P.H., TSENG, R.L., JUANG, R.S., 2010, 'Preparation of activated carbons from unburnt coal in bottom ash with KOH activation for liquid-phase adsorption' *Journal of Environmental Management*, 91: 1097-1102.

YAGMUR, E., OZMAK, M.AKT AS, Z., 2008, 'A novel method for production of activated carbon from waste tea by chemical activation with microwave energy' *Fuel* 87: 3278-3285.

YALCIN, M., AROL, A.I., 2002, 'Gold cyanide adsorption characteristics of activated carbon of non-coconut shell origin,' *Hydrometallurgy*, 63: 201.

- YAVUZ, G., ZEKI, A., 2014, 'Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol' *Applied and Surface Science*, 313:352-359
- YEGANEH, M. M., KAGHAZCHI, T., SOLEIMANI, M. 2006, 'Effect of raw materials on properties of activated carbons' *Chemical Engineering and Technology*, 29(10): 1247–1251.
- YIN, C. Y., AROUA, M. K. DAUD, W. M. A. W., 2007, 'Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions' *Separation and Purification Technology*, 52: 403-415.
- YOUSSEF, A.M, EL-NABARAWY, TH. EL-SHAFFEY, E.I, 2006, 'Modified activated carbon from olive stones for the removal of heavy metals' *Carbon Science* ,7(1): 1-8.
- ZADRA, J.B., ENGEL, A. L., HEINEN, H.J. 1952, 'Process for recovering gold and silver from activated carbon by leaching and electrolysis' *U.S.B.M.* RI 4843.
- ZHANG, F.S., NRIAGU, J.O., ITOH, H., 2005, 'Mercury removal from water using activated carbons derived from organic sewage sludge' *Water Research*, 39 (2-3): 389-395.
- ZHANG, N., LIN, L.S., GANG, D, 2008, 'Adsorptive selenite removal from water using iron-coated GAC adsorbents' *Water Research*, 42 (14): 3809-3816.
- ZHANG, J., FU, H., LU, X., TANG, J., XU, X, 2011, 'Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process' *Biomass and Bioenergy*, 35: 464-472.

ZHANG, J., GIORNO, L., DRIOLI, E., 2006, 'Study of a hybrid process combining PACs and membrane operations for antibiotic wastewater treatment' *Desalination*, 194 (1-3): 101-107.

ZHAO, J., YANG, L., LI, F., YU, R., JIN, C., 2009, 'Structural evolution in the graphitization process of activated carbon by high-pressure sintering' *Carbon*, 47: 744-751.

ZHU, Z., LI, A., YAN, L., LIU, F., ZHANG, Q., 2007, 'Preparation and characterization of highly mesoporous spherical activated carbons from divinyl benzene-derived polymer by ZnCl_2 activation' *Journal of Colloid and Interface Science*, 316: 628-634.

ZUO, S., YANG, J., LIU, J., CAI, X., 2009, 'Significance of the carbonization of volatile pyrolytic products on the properties of activated carbons from phosphoric acid activation of lignocellulosic material', *Fuel Processing Technology*, 90: 994-1001.

