

**A COMPARATIVE STUDY ON THE UTILIZATION OF *BERCHEMIA*
DISCOLOUR SEED SHELL CARBONS AND HAYCARB CARBON FOR**

GOLD RECOVERY



by

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DEDICATION

This thesis is dedicated to my warmhearted parents and siblings who would unceasingly pray for this project to be a success. More gratitude is conveyed to Mr Mamvura, the Jena Mines Mine Manager who facilitated the main chemicals and most of the costs incurred during the course of the thesis and to Jena Mines itself for mentoring me in this area of specialty. Above all I thank Jehovah for giving me strength in conducting this research.

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- Mr T. Nharingo (Project main supervisor)
- Dr U. Guyo (Project co-supervisor)
- Dr M. Moyo (lecturer)
- Evidence Mtetwa (student)

ABSTRACT

A comparative analysis of the efficiency of activated carbon produced from *Berchemia discolor* seed shells derived activated carbon (BDSAC) and commercial grade activated carbon (Haycarb Carbon) was utilized in the adsorption of gold (iii) chloride from acidic medium. The adsorption process of BDSAC was best described by the Freundlich, Halsey, Dubinin-Radushkevich (D-R), Temkin isotherms and Langmuir isotherm had R_L values in the range $0 < R_L < 1$ hence the adsorption process was favourable. The pseudo-second order, Spahn and Schlünder and Intra-particle diffusion kinetic model best described the kinetics implying that the rate-limiting step is sorption concerning valency forces through redox reaction between Au^{3+} and BDSAC dependent on the external diffusion of Au^{3+} in solution to BDSAC and the intra-particle diffusion of the molecules through a boundary layer of thickness 0.7042. The maximum removal capacity was determined as 100 % at an ionic strength of 0 M $NaNO_3$, adsorbent dosage of 0.002 g/L and an initial concentration of 10 ppm. The removal capacity of Haycarb Carbon was also 100 %. BDSAC was found to be an efficient adsorbent as evidenced from its Freundlich exponent.

Key words: *Berchemia discolor*; gold, Haycarb, carbon.

DECLARATION

I, **Kudzai Jinjika** R131211P, hereby declare that I am the sole author of this dissertation. I authorize Midlands State University to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature.....

Date.....

APPROVAL

This dissertation entitles “**A comparative study on the utilization of *Berchemia discolor* seed shell carbons and Haycarb carbon for gold recovery**” by **Kudzai Jinjika** meets the regulations governing the award of the degree of **Bachelor of Science in Chemical Technology Honours** of the Midlands State University, and is approved for its contribution to knowledge and literal presentation.

Supervisor

Date

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LIST OF ABBREVIATIONS

BDS – *Berchemia discolor* seed shells

BDSAC – *Berchemia discolor* seed shells activated carbon

AC – Activated carbon

CHAPTER 1

INTRODUCTION

1.1 Background

Gold is one of the pricey and precious heavy metals with its exploitation extending from units of exchange and a symbol of wealth [1–3]. To date, gold is being used in electronics, medicine, engineering and catalysis [1]. The mining activities for gold extraction have been in practice for a long time, dating from 3050 BC by methods of cementation [3], precipitation [4], solvent extraction [3], ion exchange [5] and adsorption [6,7]. Amongst the numerous methods employed in the preconcentration of trace gold (III), solid phase extraction (SPE) has unparalleled performance relative to other methods because of its superiority in high enrichment factor, low cost, low consumption of organic solvents, rapid phase separation, high recoveries and its capability to be combined with different detection techniques online or offline [2,3].

With SPE processes, a variety of solid phases have been employed in the recovery of gold (III), such as goethite [8], albite [7], L-arginine modified silica [9], resin [10] and activated carbon [6]. According to recent studies, activated carbon has been the most preferred adsorbent because of its high adsorptive capacity, high adsorptive rate, high mechanical strength and wear resistance, simple reactivation procedures and uniform particle size distribution [11–13]. Activated carbon (AC) is a porous and carbonaceous solid material that is prepared by carbonizing and activating organic substances [14,15].

Some of the organic substances used for the synthesis of activated carbon are wood, coal, coconut shells, bones and rubber [16,17]. The use of these materials without their surface treatment gives poor adsorption capacities for metal ions and thus they need to be carbonized or

activated or both. The chemical method of activation is a single step process for the preparation of activated carbon from organic precursors in the presence of chemical agents as both carbonization and activation take place in a single step [18]. Carbonization involves the chemical treatment of the lignocellulosic precursor with acids like concentrated sulphuric acid (H_2SO_4) and nitric acid which are powerful dehydrating agents. They react with organic compounds, removing water and degrading the precursor to elemental carbon. This process promotes the degradation of the cellulose and hemicellulose fractions leaving behind a modified lignin residue [19].

In activation, the aim is to form surface oxygen groups on the precursor which are active in the adsorption process by heating the carbonaceous material. These functional groups bind to specific metals and in the case of gold extraction, are oxidized as the gold is reduced in solution [20].

Agricultural wastes have been utilized in the production of activated carbon. At large, physically activated coconut shells have been utilized because the carbon cycle of the coconut shell activated carbon is for a couple of months because it is hard, has small macroporous structure, high fixed carbon content and low ash content [21]. Unfortunately, this carbon type is imported from countries like Netherlands, Sri Lanka and Indonesia, well known as Haycarb carbon and it is very expensive [22]. Recent studies suggest venturing into the use of other agricultural wastes to prepare activated carbon that exhibits properties parallel to those of coconut shell activated carbon for example walnut shells [23], vine shoots [24], olive stones [25], apricot kernel [16].

Berchemia discolor seed shells (BDS) have not been used for any cited adsorption studies yet they are an agricultural waste capable of exhibiting the required qualities and can also exhibit the

same adsorption-desorption characteristics comparable to those of coconut shell activated carbon. As such, this is a cheaper process as the use of the seed shells employs chemical activation which is more economic than physical activation for commercial coconut shell activated carbon.

This has led to the initiative to utilize the *Berchemia discolor* seeds shell activated carbon (BDSAC) since the seeds shells exist in abundance in Southern Africa and are thus cheap to employ [26]. The utilization of this substance avoids the need to import Haycarb carbon [27] and significantly enhances the economic and environmental sustainability of the gold extraction process since the waste is employed in a beneficial manner.

1.2 Problem statement

The extractive metallurgy of gold is becoming increasingly costly in Zimbabwe and other Southern African countries because gold complexes are being encountered as mining goes deeper into the ground and are expensive to process. Initially, gold existed in its native form and now it is associated with tellurides and stibnites (AuTe_2 and AuSb_2 respectively) thus adding a cost to the extraction [28]. More to that, Haycarb carbon is the prominent carbon source owing to its high adsorption capacities and durability because of the source of the precursor which are coconut shells [22]. As such, it is thus imperative to look for means to reduce the costs incurred so that maximum profits can be made.

1.3 Aims

- ✚ Development of activated carbon granules from a natural lignocellulosic precursor (BDS) using H_2SO_4 and HNO_3 as activating agents.
- ✚ Recovery of gold (III) from chloride media using activated BDSAC and Haycarb carbon.

1.4 Objectives

- ✚ To prepare activated carbon from BDS using H_2SO_4 and HNO_3 .
- ✚ To characterize the activated carbon using FTIR.
- ✚ To determine the pH at point of zero charge of BDSAC.
- ✚ To determine the optimum pH, dosage, contact time, temperature, ionic strength and to determine the effect of initial concentration on the adsorption of gold (III) onto the BDSAC
- ✚ To determine the optimum contact time and to determine the effect of initial concentration on the adsorption of gold (III) onto Haycarb Carbon.
- ✚ To compare the adsorptive capabilities of BDS activated carbon (BDSAC) and Haycarb carbon.

1.5 Justification

Berchemia discolor seeds shells are an abundant hard agricultural waste which have not been used in any adsorption study yet they are abundantly found in the Southern African region where Zimbabwe is located. Since it is a waste product and yet, hard when carbonized and activated and also has adsorptive capacities paralleled to those of Haycarb carbon, it is imperative to utilize it in gold recovery as this will significantly reduce the costs of extracting gold.

1.6 Limitations

The main obstruction in carrying out the thesis was on the unavailability of analytical instruments which would give detailed information the structure of the adsorbent before and after adsorption and also elaborate on the mechanism of adsorption. Instruments which were required are the scanning electron microscope (SEM) and the transmission electron microscope (TEM) to investigate the morphology and dimensions of the adsorbent .X-ray photoelectron spectroscopy (XPS) would be used to identify the species of gold on the adsorbent surface.

1.7 Delimitations

The functional groups of the adsorbent were determined using the Fourier Transform Infrared Spectroscopy (FTIR). This was carried out before and after adsorption to determine the functional groups that took part in the interaction of the gold complex and the adsorbent.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter gives an insight into the importance of gold (III), its methods of extraction, how it is extracted using different adsorbents and the need to employ the novel adsorbent *Berchemia discolor* seed shells activated carbon (BDSAC). The last part of the chapter -focuses on the types of adsorption isotherms that were employed in the adsorption process.

2.1 The uses of Gold (III)

Gold is one of the most precious metals and it does not react with sulphur or oxygen. Its durability under the most corrosive conditions has made it be applicable in widespread applications like coinage and jewelry over a long time [29,30].

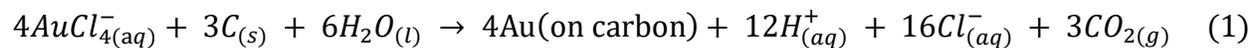
2.2 Recovery of Gold (III) from solution

The gold in chloride solution as AuCl_4^- has to be isolated from other metals and impurities in the solution so that it can be refined and purified. There are several methods employed for this reason and they are mentioned below.

2.2.1 Carbon Adsorption

This process, usually identified as the carbon in pulp (CIP) process applies granular activated carbon in the separation of gold from the leached pulp [31]. Usually, coconut shell activated carbon is utilized because of its favorable characteristics of durability and very high adsorption capacities for gold [27]. Variations to this method are the Carbon-in-leach (CIL) and Carbon-in-Column. The CIL process involves first filtering the pulp into a clear solution then adding activated carbon for adsorption to take place. The CIC process involves placing the activated carbon in a column in which the leached pulp or solution will flow through and the gold is adsorbed [32].

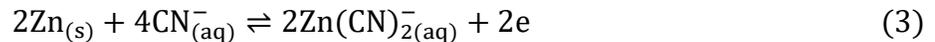
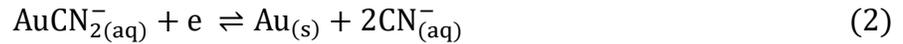
In the CIP process, the activated carbon is placed in a series of agitating tanks in a counter-current flow arrangement in which they will be in contact with the pulp for a particular retention time. It is then screened from the pulp using a vibrating screen, is stripped of the gold (elution), regenerated and recycled back into the system. This technique is employed on low grade ores. The adsorption of gold (III) chloride onto activated carbon occurs via the reaction shown in equation 1 [32];



The concentrated gold solution from the eluate solution passes through electrowinning cells where the gold and other metals report to the cathodes. The cathodes are then washed with dilute sulphuric acid to dissolve residual zinc and copper if any. The cathodes with gold are then taken for smelting where the gold is purified and collected as a solid bar [32].

2.2.2 Cementation (Merrill Crowe Process)

By improvising the standard reduction potentials of any reductant and comparing them to the corresponding half reaction of gold reduction, if it is lower than that of gold, the reductant can be used to reduce gold to its metallic state. Utilizing zinc as the reducing agent, the cementation of gold from solution was developed in 1890 for removal of gold from cyanide solutions. The pregnant solution is isolated from the ore by filtration and counter-current decantation (CCD) then is clarified in clarifiers. A vacuum deaeration column is employed in the removal of oxygen from the solution then zinc dust is added to the solution. Gold is then precipitated from the solution because zinc has a higher affinity for cyanide than gold [32]. The reactions that occur are shown in equation 2 and 3



The precipitate is filtered from the solution, mixed with fluxes then smelted to remove impurities. This method is preferred if the ore has high silver content because the CIP process will require large carbon stripping and electrowinning sections to process the large quantities of silver. The rule of thumb states that the economic gold to silver ratios greater than 4:1 favor the installation of the Merrill-Crowe process if the ore has low settling rates. The drawbacks of this method are that it is prone to high metal consumption or passivation by metal sulphides on the metal cement surface [33].

2.2.3 Ion Exchange

This involves the use of an inert polymeric hydrocarbon matrix, usually synthesized from polystyrene cross-linked with divinyl benzene where functional groups are chemically attached. The matrix is a three-dimensional matrix and swells when in contact with aqueous solutions by the absorption of water and the ions in the solutions diffuse through the gel to the functional groups which can be anionic or cationic. The rates of exchange are high, reversible and generally diffusion-controlled and the selectivity of the resins are dependent upon the size, polarizability and charge of the ions in solution [32].

In hydrometallurgy, gold is present as an anionic complex thus anionic exchange resins are employed more often in gold metallurgy. Their important traits are their selectivity for auric chloride because there will be different other anions in the leach liquor and the competition of these anions have a significant influence on the gold extraction efficacy [34].

The elution of gold from the resins is achieved by treating them with a dilute solution of sodium hydroxide. If coupled with electrolysis 99 % of the gold is eluted using 0.5 M NaOH or ethanol in less than 4 hours [35]. The efficiency and simplicity of this method offers advantages for the implementation of ion exchange in gold hydrometallurgy. On the contrary, the advantage of this method has to be weighed against their low capacity at higher pH. The disadvantage lies in the pulverization of the resin with time [33].

2.2.4 Solvent-extraction process

This method was initially employed in the extraction of Uranium and now is being used for the copper, zinc, vanadium and other platinum- group metals. In solvent extraction, a large amount

of organic solvent is used to extract metal ions from a solution in which they are found and stripping is done afterwards. The composition of the organic solvent determines the distribution of the metal in it. The solvent can be purely organic or ordinarily an organic reagent in a diluent that is inert [36]. Solvent extraction can be subdivided into three categories depending on the type of reactions that occur during extraction [8];

Physical Distribution – when there is no chemical reaction but a mere molecular arrangement of the solute between the inert solvent and aqueous phase. Such occurrences are not frequent and occur when the solvent is not carefully solvated in the aqueous phase.

Solvation – this is employed for neutral species and entails the transformation of the metal cation into a form that can dissolve in the organic phase. The extractant molecules replace the water molecules that the metal has therefore making it more soluble. Types of extractants used are ethers, alcohols and ketones. The extraction of auric chloride is an example to which this method is employed.

Anion Exchange – a cation is utilized for the extraction of an anionic metal in the ion pair form after a non-metallic anion has been interchanged between the organic and aqueous phase. The cationic part of the ion pair is formed by protonation of a weak basic compound, usually a nitrogen containing base such as an amine or it can be from a quaternary ammonium. The recovery of gold from cyanide, thiocyanate or chloride leach liquors are treated by this method.

Cation Exchange – in this process, a complex metal cation or a hydrated metal cation is formed by the displacement of another cation. The reaction can involve chelation and chemical bonding of the extractant and the metal ion or rather an electrostatic interaction between the anionic extractant and a metal cation. If in some case the cation displaced is a hydrogen ion, the reaction

will then depend on the pH of the solution. This phenomenon makes it possible for gold recovery from a thiourea leach liquor by cation –exchange solvent extraction.

Solvents used for the separation of gold chloride from PGM are dibutyl carbitol and methyl isobutyl ketone. The problems with the solvent extraction methods are in disposing hazardous waste and incomplete gold extraction.

2.2.5 Electrowinning

It is also called electroextraction and it is the electrodeposition of metals from their solutions after they have been extracted from their ores. Its application is mainly focused on concentrated liquors. An electric current is passed through the solution and the gold reports to the porous cathodes which are then washed with dilute sulphuric acid to remove metal such as copper and iron prior to smelting [32]. Electrowinning has acquired nominal attention due to its low current densities and low current efficiencies experienced with low gold concentrations.

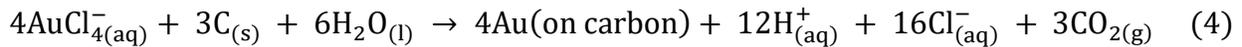
In summary, amongst all the extraction methods, adsorption has unparalleled performance considering efficiency and being enviro-friendly as other methods mentioned above suffer high energy requirements, generation of toxic sludge or waste products, incomplete metal removal and costly reagent requirements [9].

2.3 Adsorption Aspects

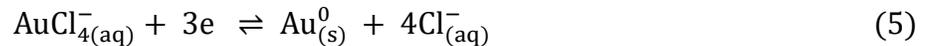
Adsorption is a low cost and important physical process [17] involving the accumulation of molecules at the surface rather than in the bulk. It is divided into physisorption in which the interactions are dominated by Van Der Waals forces between the adsorbate and adsorbent and chemisorption when the adsorbate chemically bonds to the adsorbent.

2.4 Mechanism of adsorption of gold (III) chloride onto activated carbon

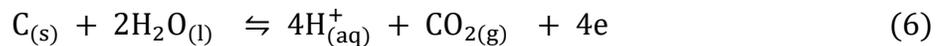
In gold (III) chloride containing solutions, a chemical reduction reaction occurs at the surface of the activated carbon and metallic gold forms on the carbon surface simultaneously producing carbon dioxide as shown in equation 4 [6].



The mechanism of adsorption involves the reduction of Au(III) to metallic gold on the surface of the carbon with the relevant reactions shown in equation 5:



The reducing electrons are supplied by the activated carbon as shown in equation 6



Gold deposition from chloride solutions is said to occur at suitable sites to form spherical particles of 0.5 to 35 μm and distributes itself to form a metallic gold surface. The rate is controlled by boundary layer diffusion and is not sensitive to the initial gold concentration [6]. It is also independent of pH when the pH is below neutral and decreases significantly as the pH exceeds the neutral point. The gold metal is not also deposited in the whole carbon granule but only on the surface in the large pores open to the bulk solution [37].

2.5 Properties of Activated Carbon

Activated carbon, or charcoal as it is now less commonly called is an organic material of graphitic structure with a highly developed internal pore structure, large specific surface area and tunable surface oxygen containing groups [38]. Due to all these features, it has been employed in several industrial applications and one of these is in gold extraction.

The physical factors of activated carbon that are vital for gold extraction according to Soleimani and Kaghazchi [39] are;

- ✚ High adsorptive capacity – to utilize nominal amounts of activated carbon in a system for gold adsorption
- ✚ High adsorption rate – to enable the system to reach equilibrium early and make the process less time consuming and more economic.
- ✚ High mechanical strength and wear resistance – to withstand the forces imposed by abrasion and attrition upon collisions with impeller blades and other members of the system
- ✚ Simple reactivation methods – to enable efficient and economic reactivation of the activated carbon.
- ✚ Uniform particle size distribution – to ensure uniform distribution and easy transfer of the carbon from one tank to the other via vibrating screens.

Cost, availability and service by supplier are some considerations that are not technical yet relevant [40].

2.6 Manufacture and activation of carbon

Activated carbon is manufactured from the carbonization and activation of organic precursors. This is so because an organic material in its raw state cannot efficiently adsorb if at all any metal ions. Virtually any carbonaceous material can be utilized in the synthesis of activated carbon extending from cassava peels [41], wood [42], anthracite [43], coconut shells [44] and tree leaves [45] as those of peaches. The type of raw material used has a significant implication to the characteristics of the produced activated carbon [46].

Methods of manufacturing activated carbon are divided into two categories, the chemical and physical activation methods. These methods can be implemented after the chosen precursor is carbonized or carbonization can be done in unison.

2.6.1 Carbonization of the precursor

Carbonization is performed to lower the volatile contents of the precursor so that it is converted into a suitable form for activation [47]. Usually, the carbon content of the precursor should surpass 80 % [48]. During carbonization, the carbon atoms arrange into the desired graphitic structure. The succeeding step of activation, either chemical or physical serves the same role of enhancing the low adsorption properties of the carbon and is ultimately pore development through chemical reactions. Usually carbonization is done using sulphuric acid, nitric acid, hydrochloric acid or phosphoric acid [25].

2.6.2 Physical Activation

In physical activation, carbonization or calcination occurs at very high temperatures (800-1 000 °C) in the presence of activating agents or gases that oxidize the substance like carbon dioxide, steam or a mixture of the two gases. After this, the substance is subjected to mild oxidation (gasification) with steam, air and /or carbon dioxide. This drives the volatile contents which exist as fats and oils out of the substance. As this occurs, pores are formed as the volatile substances leave voids behind in the stable layers of biomass. Gasification of the substance serves to expand the pores to create mesopores. If the activation is carried out at low temperatures, the reaction will be very slow and the reactions will be taking place inside the substance yet at higher temperatures the reactions will be occurring on the outside [25]. The reaction below occurs between carbon dioxide and the carbon matrix



According to Chowdhury et al, the temperature at which activation occurs and the residence time during activation using carbon dioxide is said to be inversely proportional to the solid yield and directly proportional to the pore volume for activated carbon prepared from apricot stones [49]. At a certain temperature and time for every substance, if exceeded, the pores end up collapsing and the substance turns to ashes.

2.6.3 Chemical Activation

Unlike physical activation, this process occurs at a lower temperature. The precursor is impregnated with a dehydrating agent like concentrated sulphuric acid or nitric acid or both for dehydration to occur. The chemicals then degrade the cellulosic backbone of the precursor and

pore development occurs by oxidation and dehydration. This results in simultaneous carbonization and activation of the precursor. The volume occupied by the activation agent is directly proportional to the micropore volume of the derived activated carbon [24].

This process has higher yields than physical activation but the drawback of the process is the need to wash the activated carbon of the chemical agent until it is neutral. This requires a lot of water and base to neutralize the substance. Besides that, chemical activation has been said to be more efficient in producing fibrous activated carbons from cellulose fiber than physical activation using CO₂ [24].

2.7 Chemical factors affecting adsorption of gold (III) chloride onto activated carbon

Besides the physical factors exhibited by the activated carbon there are also chemical factors that either inhibit or enhance the rate of gold adsorption of gold(III) chloride onto activated carbon. It is therefore imperative to optimize the conditions under which adsorption occurs at a fast and economic advantage. Below are discussed the properties that affect the adsorption of gold onto activated carbon in chloride media.

2.7.1 Effect of solution pH on adsorption of gold (III) chloride onto activated carbon

This is the aspect of paramount importance in adsorption. The optimum pH is determined before all other adsorption optimizations are carried out. The hydrogen ion concentration of a solution is the most important aspect for the adsorption section because the proton in the acid can protonate the binding sites of the molecules and the hydroxide ion can complex and precipitate many metals. According to Zhang et al [2], the adsorption of Au (III) reaches a maximum of > 98 % constantly at pH values less than 3 above which hydrolysis occurs.

2.7.2 Effect of adsorbent dosage on the adsorption of gold (III) chloride onto activated carbon

As expected, as the amount of the adsorbent increases, the amount of the adsorbate should decrease as well. The gold sorption (%) also increases with the increase in sorbent dosage since the reaction of the two is thermodynamically favorable if the ratio of the sorbent to metal is high [3]. The increase in the dosage of the sorbent implies the increase in active sites for the gold atoms thus explaining the relationship. For a particular concentration of gold in solution, there is a defined maximum dosage which if exceeded, would only be a waste of adsorbent [3]. Therefore, denoting the optimum adsorbent dosage is important to make the process efficient and economic.

2.7.3 Effect of contact time on the adsorption of gold (III) chloride onto activated carbon

This is the residence time of the adsorbent in the sorbent for adsorption to occur and the more the residence time, the higher the adsorption %. The time the adsorbent is in contact with the sorbent determines the time it takes for the reaction to reach equilibrium after which increasing the contact time has no advantage to the system [3]. It is thus advisable to determine the contact time which is favorable for the system to reach equilibrium.

2.7.4 Effect of temperature on the adsorption of gold (III) chloride onto activated carbon

According to Morcali and Wojnicki [3,50]. As the temperature increases, the kinetic energy of the gold ions increases and so does the frequency of collision thus the rate of adsorption also

increases with the increase in temperature for an endothermic reaction and the contrary occurs for an exothermic reaction. The diffusion of the gold(III) is accelerated following a behavior described by the Arrhenius equation shown in equation 8 below

$$K = Ae^{-E_a/RT} \quad (8)$$

where A = constant related to collision frequency of solution species, R = gas constant $\text{JK}^{-1}\text{mol}^{-1}$, T = absolute temperature (K), E_a = activation energy for the reaction (kJmol^{-1})

2.7.5 Effect of ionic strength on the adsorption of gold (III) chloride onto activated carbon

As the ionic strength increases, it implies that there are more ions competing for the adsorption sites on the activated carbon. As the concentration of the other ions increases they tend to shield the gold ions from the carbon adsorption sites and the adsorption of the gold complexes reduces significantly with the increase of other ion [51]. The changes in metal adsorption with ionic strength can serve as a method to distinguish between inner and outer-sphere complexes [51]. Inner-sphere complexes are not influenced by the ionic strength.

2.7.6 Effect of initial gold(II) concentration on the adsorption of gold (III) chloride onto activated carbon

The initial gold concentration has no influence on the adsorption of gold (III) chloride according to Wojniki [50] and also on their reduction to the metallic form. The adsorption capacity tends to increase with increase in initial concentration.

2.8 Review of studies carried out on activated carbon

This section covers other procedures employed in the synthesis of activated carbon from different precursors designed for gold (III) chloride recovery and the results obtained thereafter.

2.8.1 Plants used for activated carbon synthesis

In other researches, Soleimani and Kaghazchi utilized apricot stones as activated carbon precursors to adsorb gold from wastewater. The activated carbon was prepared from the apricot stones using chemical activation using phosphoric acid for carbonization at a temperature of 400 °C. It was employed in gold recovery and had a maximum loading capacity of 6.028 g interpreting to 98.15 % gold recovered in 3 hours [52] .

Buah and Williams [53] also synthesized activated carbon from coconut shells using physical activation, carbonizing the precursors with steam at 600 °C and activating the resulting chars at 900 °C. The activated carbon was used to adsorb gold and had a maximum adsorption capacity of 32.52 mg/g of gold (III) from chloride solution.

In 2015, Morcali et al [3] also studied the recovery of gold from chloride media using a different precursor as an alternative for the coconut activated carbon. The precursor was rice hulls which were activated at 1000 °C under argon atmosphere. The maximum adsorption capacity for the rice hull derived activated carbon was 93.46 mg/g.

Palm nut shells were also activated and made into a granular form for the use of adsorbing gold but in this case, from cyanide solution. Buah and Williams [54] physically activated palm nut shells by using pyrolysis first at 600 °C followed by steam activation at 900 °C. The maximum

adsorption capacity of the carbon was 56.63 mg/g for the carbons activated for 3 h and 63.04 mg/g for carbon activated for 6 h owing to the differences in porosities.

Since different methods for different precursors are available for the synthesis of activated carbon, in this study, chemical activation of the *Berchemia discolor* seeds using a mixture of acids at 125 °C was employed to produce activated carbon.

2.8.2 *Berchemia discolor* species information

These are fruits from a deciduous African tree which is found in countries like Zimbabwe, Kenya, Mozambique, Malawi, South Africa and many other countries in Southern Africa. It is in the family of Rhamnaceae and has other names it is known with like *Adolia discolor*, *Araliorhamus punctulata*, *Araliorhamus vaginata*, *Phyllogeiton discolor* and *Scutia discolor*. The other names it has which are not botanical are Brown ivory, dog plum, mountain date, wild almond, Qanantab, Jajaba, Jejeba, Deen, Dheen-den ro'o and Kor'guba [26].

Orwa et al [26] asserts that the *Berchemia discolor* tree height lies in the range of 3 to 20 meters and it has a bole that is straight. The fruit of the tree is eaten fresh or dried first and is even sold in markets. The *Berchemia discolor* tree grows naturally in different types of climates ranging from semi-arid areas to areas having rainfall in 4 out of 5 years but it is destroyed by frosts and cold wind.

The tree and its components are utilized in different manners. The fruit can be eaten raw or cooked because it has a high sugar and vitamin content. The roots have medicinal value and the bark is actually used for treating liver problems. The resin from the heartwood is used as a glue. Dyes are also made from the bark and heartwood. Since the wood is very hard, it is used for making furniture like tables, chairs, benches, poles and pestles [26].

The tree grows at the rate of 600-800 mm per year producing hard seeds of dimension 20 by 8 mm which are hard and not utilized in any manner besides planting more seeds. There are 3000-3500 seeds per kg and this much of seeds are not being utilized efficiently thus their use in adsorption industries is imperative as a substitute for coconut shell activated carbons.

This will open portals in the use of indigenous products and play an important role in reducing import costs and also enhance exportation of the product. The hard seeds have characteristics that when carbonized and activated can exhibit desirable characteristics that can relinquish the use of the expensive coconut shell activated carbon that needs to be imported yet is expensive to justify its use in developing countries like Zimbabwe.

2.8.3 Biosorbent characterization and gold determination in aqueous solutions

The characterization of biosorbents is usually carried out using the Fourier Transform Infrared Spectroscopy. In this instrument, adsorption due to the vibrational and rotational motions in the infrared region occurs and causes the functional groups of the compound to bend and stretch giving characteristic peaks at particular frequencies [55,56].

Employing a solid disc, FTIR determines the functional groups present in a given sample. The solid disc is made by mixing the organic component with Potassium bromide in the ratio 1:10. The mixture is homogenized into a fine powder by using a pestle and mortar. A small quantity is placed into a nut with the other ends being compressed manually to make a transparent disc to allow for the light to pass through. Initially, the background scan is removed from the spectrophotometer by running a disc with KBr to reduce the noise of the instrument. Afterwards the sample is then placed into the cell and is analyzed.

The amount of gold (III) ions in solution is quantified by the Flame Atomic Absorption Spectrophotometer and this ionizes the gold atoms and determines the characteristic absorbance of the metal using a gold lamp. The absorbance is related to the concentration of the gold metal ions in the solution [57].

At first, the instrument is calibrated using standards of particular concentrations. This ensures accurate and reliable results from the instrument. The samples are then run after proper calibration of the instrument and the concentrations at corresponding absorbance are produced. These denote the amount of analyte left after sorption in the solution.

2.9 Equilibrium Isotherms

The equilibrium isotherms apply specifically to a specific adsorbent and are of paramount importance in the designing of adsorption processes. They assist in illustrating the adsorptive characteristics of the adsorbent and also estimate the capacity of the adsorbent using a suitable isotherm model from the several models. The different models utilized in considering the equilibrium adsorption of compounds are Langmuir, Freundlich and Temkin Isotherms. These have certain constants that convey the surface properties and affinity of the adsorbent.

2.9.1 Linear Langmuir Isotherm

This was primitively formulated for the adsorption of gases onto solids assuming that it would be a monolayer adsorption occurring at a fixed number of localized sites on the surface with all adsorption sites superposable and equal in energy. The isotherm is thus based on assumptions of a structurally homogenous adsorbent by equation 9 below [58]

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \quad (9)$$

Where C_e = equilibrium concentration (mg/L), q_e = amount of Au^{3+} adsorbed per unit weight of adsorbents at a specified equilibrium (mg/g), q_0 = maximum adsorption at monolayer coverage (mg/g), b = Langmuir constant related to the affinity of the binding sites (L/mg) and is a measure of energy of adsorption

The essential characteristics of the Langmuir isotherm model can also be explained by a dimensionless constant separation factor or equilibrium parameter R_L defined by equation 10,

$$R_L = \frac{1}{1+bC_0} \quad (10)$$

Where b = Langmuir constant (L/mg), C_0 = initial concentration (mg/L) T

The parameter R_L indicates the shape of the isotherms. If $R_L > 1$, the adsorption is unfavorable. If $0 < R_L < 1$ the adsorption is favorable if $R_L = 0$ then the adsorption is irreversible.

2.9.2 Linear Freundlich Isotherm

This type of isotherm properly fits for heterogeneous adsorbents and is given as shown in equation 11

$$q_e = K_F C_e^{\frac{1}{n}} \quad (11)$$

Where K_F and n are Freundlich constants related to adsorption capacity and intensity respectively [59]. The isotherm is favorable when $n > 1$, linear when $n = 1$ and unfavorable when $n < 1$ [60].

2.9.3 Linear Temkin Isotherm

This is used to appraise the heat of sorption and the indirect adsorbate-adsorbate interactions on the adsorption process. It is represented as shown in equation 12 [9]

$$Q_e = \frac{RT}{b_t} \ln K_T + \frac{RT}{b_t} \ln C_e \quad (12)$$

Where T = absolute temperature (K), R = universal gas constant ($\text{JK}^{-1}\text{mol}^{-1}$), K_t =Equilibrium binding constant, b_t = constant related to the heat of sorption.

2.9.4 Dubin–Radushkevich isotherm (D-R)

It estimates the apparent porosity and adsorption energy and its linear form can be expressed as shown in equation 13 [61]

$$\ln Q_e = \ln Q_m - \beta(RT \ln(1 + \frac{1}{C_e}))^2 \quad (13)$$

where Q_e = amount of Au^{3+} adsorbed at equilibrium (mg/g), Q_m = adsorption capacity (mg/g), β = constant related to the adsorption energy, R = ideal gas constant ($\text{JK}^{-1}\text{mol}^{-1}$), T = Temperature (K), C_e = equilibrium concentration in (mg/L).

2.9.5 Halsey adsorption isotherm

It predicts multilayer adsorption and fitting of equilibrium data to the model suggests the heteroporosity of the sorbent surface. It is represented in linear form as shown below [59];

$$\ln Q_e = \frac{1}{n} \ln K_H - \frac{1}{n} \ln C_e \quad (14)$$

Where K_H and n = Halsey adsorption isotherm constants, Q_e = amount of Au^{3+} adsorbed at equilibrium (mg/g), C_e = equilibrium concentration in (mg/L).

2.9.6 Adsorption Kinetics

These are utilized in the investigation of the adsorption mechanism employing the pseudo-first order and pseudo-second order kinetic model. The intra particle diffusion model can also be applied to study the adsorption dynamics [59].

Pseudo-first-order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (15)$$

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (16)$$

Where q_e and q_t are Au^{3+} adsorption at equilibrium and time t and k_1 and k_2 are adsorption rate constants for the pseudo-first order and pseudo-second order kinetic model respectively at time t [58].

Spahn and Schlünder model is chosen to describe the external diffusion on the adsorbent:

$$\ln \frac{C_1}{C_0} = -k_{ext} t \quad (17)$$

where K_{ext} is the external diffusion coefficient, C_1 is the concentration at time t

The intra-particle diffusion model is expressed by equation 18:

$$q_i = k_p t^{1/2} + C \quad (18)$$

where k_p is the intra-particle diffusion rate constant, C is a constant related to the thickness of the boundary layer [59].

CHAPTER 3

METHODOLOGY

3.0 Introduction

This chapter provides insight into methods employed in sample handling and preparation, characterization and the adsorption studies carried out on the adsorption of gold (III) ions onto activated carbon.

3.1 Sampling, preparation and storage of *Berchemia discolor* seed shells (BDS)

BDS were collected at Chiredzi Research Station, Zimbabwe at latitude 21° 01'S and longitude 31° 33'S and placed in plastic bags. The seeds were rinsed in tap water to remove dust and dried in sunlight for 5 days. Analytical grade reagents were used in all cases. A mass of 200 g of the seeds was weighed on an electronic scale (G&G JJ224BC) and soaked in 500 mL of 1 M Hydrochloric acid in a 1 L beaker overnight [62] to remove impurities [21]. Thereafter, the samples were thoroughly washed with distilled hot water until the effluent water reached a neutral pH interpreted by the pH meter (Mettler Toledo LE409). The samples were then dried in an oven at a temperature of 110 °C for 6 h [63] to eliminate moisture and were stored in a desiccator for FTIR characterization and adsorption studies.

3.2 Preparation of standard solutions

Different serial dilutions were performed for use in the adsorption experiments and the volumes used are reported in Appendix B

3.3 Preparation of activated carbon

A mass of 400 g of the dry BDS was weighed and placed into a 1 L beaker. A volume of 400 mL of concentrated H₂SO₄ (98%, ACE Chemicals) and 200 mL of HNO₃ (55%, ACE Chemicals) were added and heated in an oven at 125 °C to form the *Berchemia discolor* seed shells activated carbon (BDSAC) [64]. The heating was carried out for 24 hours after which the sample was washed with distilled water [13] and further washed with 1 % NaHCO₃ (Skylabs) until effervescence stopped and soaked in the base for 30 minutes [55,65,66]. The BDSAC was washed again with distilled water to neutrality, dried in an oven for 2 h at 110 °C and crushed to a size range of 1.4-2.8 mm suitable for the gold processing industry [53,54]. The carbon was then dried at 110 °C for 6 h to eliminate all the moisture before FTIR characterization and the sample was stored in a desiccator [63].

3.4 Characterization Techniques

Activated carbon characterization is vital due to its applications in the adsorption systems. The characterization techniques employed in this section are the ones generally used for characterizing commercial activated carbons.

3.4.1 BDS and BDSAC FTIR analysis

A mass of 0.005 g of each of BDS and BDSAC was separately mixed with 0.500 g of KBr (spectroscopic grade) and crushed using a pestle and mortar to very fine powders. The samples were dried in an oven at 110 °C for two hours and placed in a manual hydraulic press to make a diaphanous disc. The disc was then taken for FTIR (Nicolet 6700, Thermo Scientific, USA) analysis to determine the functional groups present in the frequency range of 400 cm^{-1} and 4 000 cm^{-1} [55].

3.4.2 Determination of pH at point of zero charge (pH_{Pzc})

The point of zero charge was determined by a technique described by Bouchelkia et al [67]. A mass of 0.1 g of the BDSAC was added to a series of 100 mL conical flasks with 50 mL deionized water whose pH was adjusted to 2,4,6,8 and 10 by addition of 0.1 M HNO_3 or 0.1 M NaOH denoted (pH_i) and their potential was noted. The conical flasks were placed in a water bath shaker for 24 h set at 25 °C. The dispersions were filtered and the final pH of the solutions (pH_f) and their potentials was determined.

3.5 Adsorption studies

These are of paramount importance and are necessary to enable the optimum conditions to be established for the adsorption to occur at a fast and economic rate. The adsorption processes are carried out in different chemical conditions until the environment appropriate for adsorption is determined.

The adsorption of Au(III) on activated carbon was conducted using 0.1g of the BDSAC with 50 mL [39] of 10 ppm of initial gold(III) concentration [68]. The experiments were carried out in a water bath shaker at controlled temperature (25 °C) for a period of 24 h at 300 rpm using conical flasks containing 50 mL of the 10 ppm gold (III) chloride solution [39]. Samples were taken out at regular intervals and the residual concentration in the solution was analyzed using atomic-absorption spectroscopy (AAS) by the Thermo-Scientific AAS Spectrometer (ice 3000 series) after filtering the adsorbent with Whatman filter paper number 1 to make it carbon free.

The mass of solute adsorbed per mass of adsorbent at equilibrium (q_{eq}) in mg/g was calculated using the equation

$$q_{eq} = \frac{(C_0 - C_{eq})V}{M} \quad (21)$$

where C_{eq} is the final adsorbate concentration in solution at equilibrium (mg/L), C_0 is the concentration before adsorption (mg/L) , V is the volume of the adsorbate (L) and M is the mass of the adsorbent (g).

3.5.1 Investigation of the effect of pH on gold (III) chloride adsorption onto activated carbon

The pH of the gold (III) chloride solution was adjusted to 2,4,6,8 and 10 in separate conical flasks by 1 M NaOH and 1M HCl and the BDSAC was added into the flasks [27]. They were then left in the water bath shaker (ZWY-110X30) for 24 h at 300 rpm and filtered using gravity filtration. The filtrate was taken for analysis using the FAAS.

3.5.2 Investigation of the effect of adsorbent dosage on gold (III) chloride adsorption onto activated carbon

The effect of adsorbent dosage was executed by varying the concentration of the adsorbent placing different masses of 0.05, 0.20, 0.40, 0.60, 0.80, 1.00 and 2.00 g in separate conical flasks which contained the gold (III) chloride solution at 10 ppm [55,69] with their pH adjusted to the optimum pH of 2.16. The samples were left in the water bath shaker for 24 h at 300 rpm and the filtrate was taken for FAAS analysis.

3.5.3 Investigation of the effect of contact time on gold (III) chloride adsorption onto activated carbon

At the optimum pH of 2.16, fourteen conical flasks had 0.1 g of BDSAC added with the gold (III) chloride solution of 10 ppm. They were placed in a water bath shaker at 300 rpm and had their adsorbents filtered out after 2, 4, 6, 8, 10, 12, 15, 30, 60, 90, 120, 150, 180 and 360 minute intervals [68]. The filtrate was taken for FAAS analysis to determine the amount of gold in the solutions.

3.5.4 Investigation of the effect of temperature on gold (III) chloride adsorption onto activated carbon

The effect of temperature was carried out at four different temperatures. At an adjusted pH of 2.16, BDSAC was added to the 10 ppm gold (III) chloride solution and the water bath shaker had its temperature set at 25, 30, 50 and 75 °C for 24 h [40]. After the set time of 24 h, the adsorbent was filtered out and the filtrate was taken for analysis using the FAAS.

3.5.5 Investigation of the effect of ionic strength on gold (III) chloride adsorption onto activated carbon

The effect of ionic strength on the adsorption of Au^{3+} onto BDSAC was determined by adjusting the ionic strength of the solutions using NaNO_3 at concentrations of 0.00, 0.01, 0.05, 0.1 and 0.5 M at the predetermined optimum pH [8]. The samples were placed in the water bath shaker and after a preset time of 24 h, the adsorbent was filtered out and the filtrate taken for FAAS analysis.

3.5.6 Investigation of the effect of initial Au^{3+} concentration on gold (III) chloride adsorption onto activated carbon

The effect of the initial Au^{3+} on its adsorption onto activated carbon was investigated by altering the initial concentration to 3, 6, 9, 12, 15, 20, 25, 30, 50 and 100 ppm, adjusting the pH to the optimum values 2.16 [33] using a volume of 40 mL from the prepared 10 ppm solution. A volume of 10 mL of the solution before adsorption was set aside for initial concentration determination. The adsorbate and adsorbent were placed in the water bath shaker for 24 h. The heterogeneous mixtures were filtered using gravity filtration and the filtrate was collected for analysis using FAAS.

Chapter 4

Results and Discussion

4.0 Introduction

This chapter entails the results obtained from characterization of the *Berchemia discolor* seeds before and after the adsorption of gold (III) chloride, the optimization of pH, contact time, dosage and the effect of initial concentration. The results are presented in tabular and graphical forms. The adsorption of gold (III) ions was explained by the five sorption isotherms Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halseys isotherms. Kinetic models used to describe the adsorption mechanism of the Au^{3+} are the pseudo-first order kinetic model, pseudo-second order kinetic model, Spahn and Schlünder model and the intra-particle diffusion model.

4.1 Characterization of *Berchemia discolor* seeds activated carbon

Fourier Transform Infrared Spectrophotometer (Nicolet 6700) was employed in the determination of functional groups of the raw sample and carbon sample before and after adsorption. The raw BDS sample was characterized and had 7 main functional groups. The wide peak at 3431.4 cm^{-1} can be typically attributed to the O-H stretching groups in the sample [70]. The band located at 2923.37 cm^{-1} is ascribed to the stretching of the methyl groups [71], that at 1746 cm^{-1} belongs to the carbonyl groups in the seed and these disappeared after activation [23]. The band at 1632 cm^{-1} is attributed to the stretching vibrational bands of C=O (in -COO) or C=C centering [66]. The peak at 1453 cm^{-1} corresponded to the NH in plane bend and CN stretching vibrations (amide) or stretching of C=O in carboxylic groups [72]. The band at 1122.31 cm^{-1}

represents the stretching of the C-O bonds in hydroxyl and phenol groups [13,21] and finally that at 629.53 cm^{-1} is the C-H out of plane bending in benzene derivatives [73] or wagging N-H [72]. The FTIR spectra of the BDS, BDSAC and commercial Haycarb carbon are shown in the Figure 4.1 below.

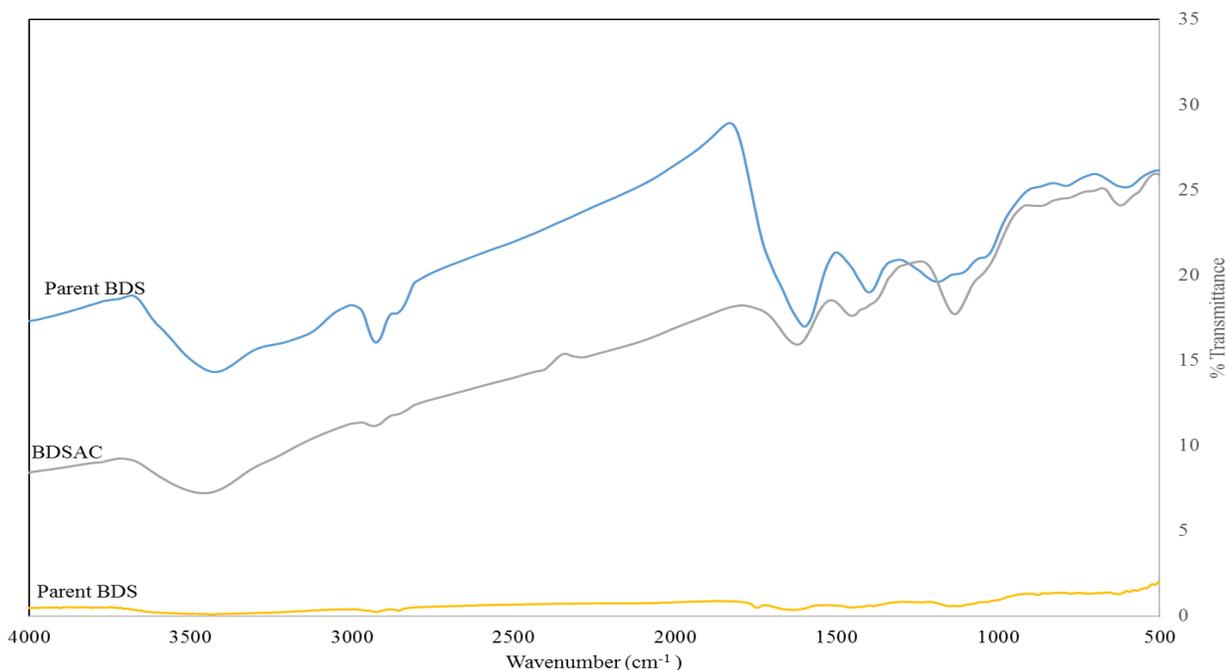


Figure 4.1.0: FTIR spectrum of (a) Parent / Raw BDS, (b) BDSAC and (c) BDSAC with adsorbed Au^{3+}

The FTIR spectrum of activated BDS shows a significant difference in the bands of the two samples meaning that the carbonization using sulphuric and nitric acid was successful. All the functional groups of the raw sample significantly changed, with one peak at 2923.37 cm^{-1} disappearing from the BDS sample after activation meaning that the aliphatic component of the raw material reacted with the acids. Another peak at 1746.32 cm^{-1} representing the carbonyl group also disappeared during thermal treatment. The BDSAC has a new peak at frequency

1384.71 cm^{-1} , this corresponds to the C-N stretching vibrations and N=O stretching of N=O bending of the tertiary amino and nitro groups respectively [34]. The new peak was as a result of the reaction of the precursor with HNO_3 . The rest of the bands in BDSAC are a slight shift from the bands of the raw BDS implying that they interacted with the chemical activation process properly.

After sorption, there was a new peak at frequency value of 2924.93 cm^{-1} , according to Yang and Qui, this might be as a result of C-H vibrations in methyl and methylene groups [23,74]. Another peak at a lower frequency of 1599.11 cm^{-1} was also recognized and this can be as a result of stretching vibrations of bonds in the aromatic ring coupled to that of highly conjugated carbonyl groups (C=O) [13]. The appearance of these functional groups after sorption implies that they took part in the metal binding process [75].

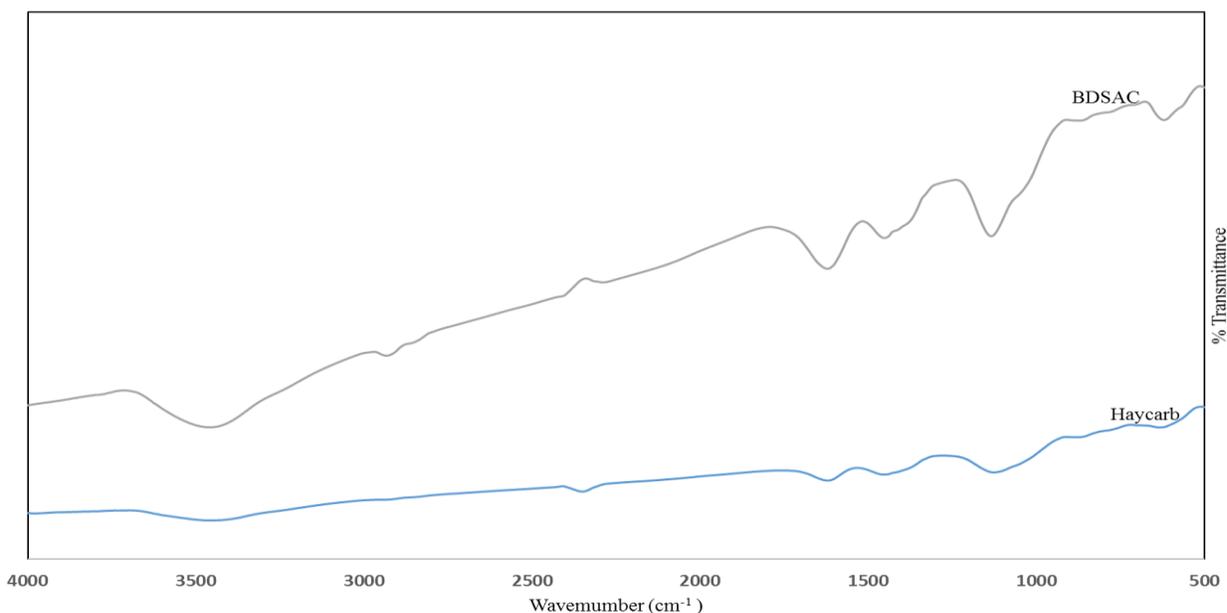


Figure 4.1.1: FTIR spectra of (a) BDSAC and (b) Haycarb carbon

Comparing the spectra of the BDSAC and Haycarb as shown in Figure 4.1.1 above, it is noteworthy that they have the same functional groups at 3463.34 cm^{-1} and 3449.61 cm^{-1} representing the phenol group. The same functional groups are also at 1628.58 cm^{-1} and 1628.13 cm^{-1} denoting the carboxylic group, 1444.12 cm^{-1} and 1448.94 cm^{-1} presenting the amide group. The frequency of transmission at 1130.88 cm^{-1} and 1120.10 cm^{-1} represents the hydroxyl and phenol groups and that at 622.17 cm^{-1} and 621.92 cm^{-1} represent the benzene derivatives respectively. The discord arises at 1384.71 cm^{-1} for the tertiary amino and nitro groups for the BDSAC implying that the Haycarb carbon type was not activated using HNO_3 . At a frequency of 2362.33 cm^{-1} for Haycarb carbon type, the frequency denotes $\text{C}\equiv\text{C}$ stretching vibrations in alkyne groups [23] which appears in the heating process.

It can be noted that the BDSAC has the hydroxyl, nitrate, amino, carboxyl and carbonyl groups as oxygenated surface functional groups.

4.2.1 The pH at point of zero charge determination

The point of zero charge was determined graphically as shown in Figure 4.1.2 after experimental procedures as 3.581. This implies that at $\text{pH} < 3.581$ the surface of the BDSAC would be positively charged and at $\text{pH} > \text{pH}_{\text{PZC}}$ then the surface would be negatively charged. Since the adsorption process involves the adsorption of a negatively charge ion, the pH below the point of zero charge was employed to avert electrostatic repulsion of the adsorbate from the adsorbent.

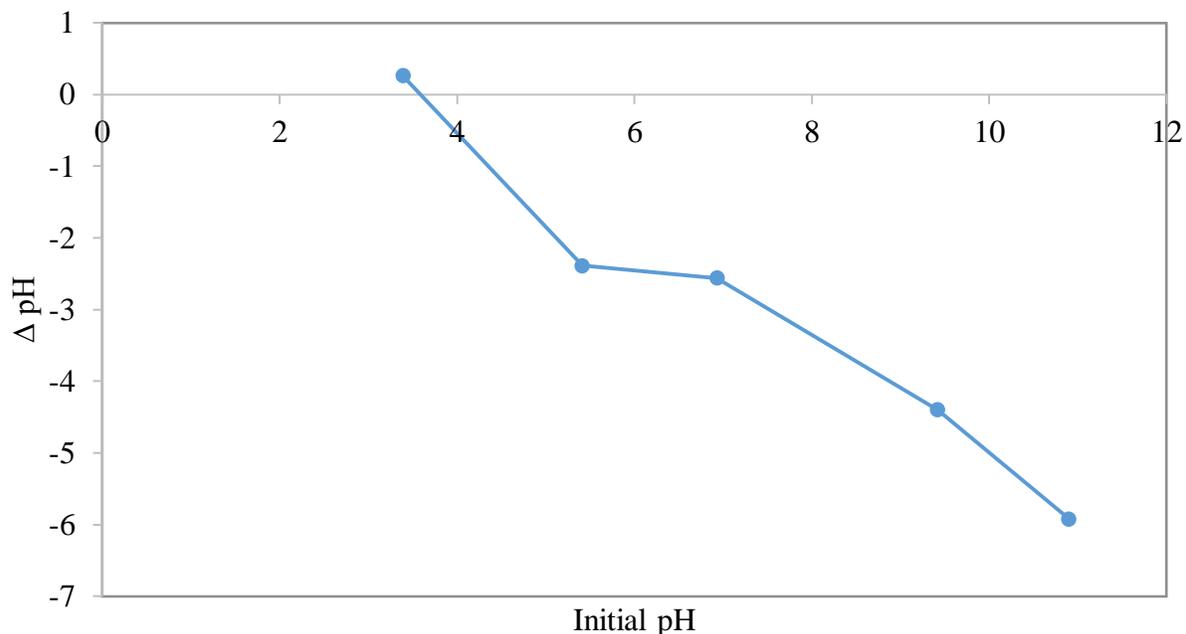


Figure 4.1.2: pH at point of zero charge determination

4.2.2 Effect of pH on gold (III) chloride adsorption onto activated carbon

The maximum concentration of gold was attained at a pH of 2.16 as shown in Figure 4.1.3 which is consistent with literature [34]. The percentage recovery at that pH was 98.79%. According to Ramesh et al [51], the pH at the point of zero charge of the adsorbent is used to explain the effect of pH on the adsorption of Au(III). The point of zero charge was determined as 3.5814 in Figure 4.1.2. He asserts that at $\text{pH} < \text{pH}_{\text{PZC}}$, the surface of the modified precursor is positively charged and at $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of the modified precursor is negatively charged. Consequently, due to the net positive charge of BDSAC at $\text{pH} < \text{pH}_{\text{PZC}}$, it attracts the chloro-anionic species of gold resulting in the greater amounts of adsorption at low pH since the precious metal, Au^{3+} is reported to be negatively charged in the presence of hydrochloric acid [30]. On the contrary, as $\text{pH} > \text{pH}_{\text{PZC}}$ the surface of the precursor increasingly becomes more negatively charged there will be a resultant repulsion with the chloro-anionic complex since they will be having the same

charge. Consequently, the Q_e reduced with an increase in pH . Thus, the optimum pH for gold(III) chloride sorption onto BDSAC is pH 2.16 with a recovery of 98.79%.

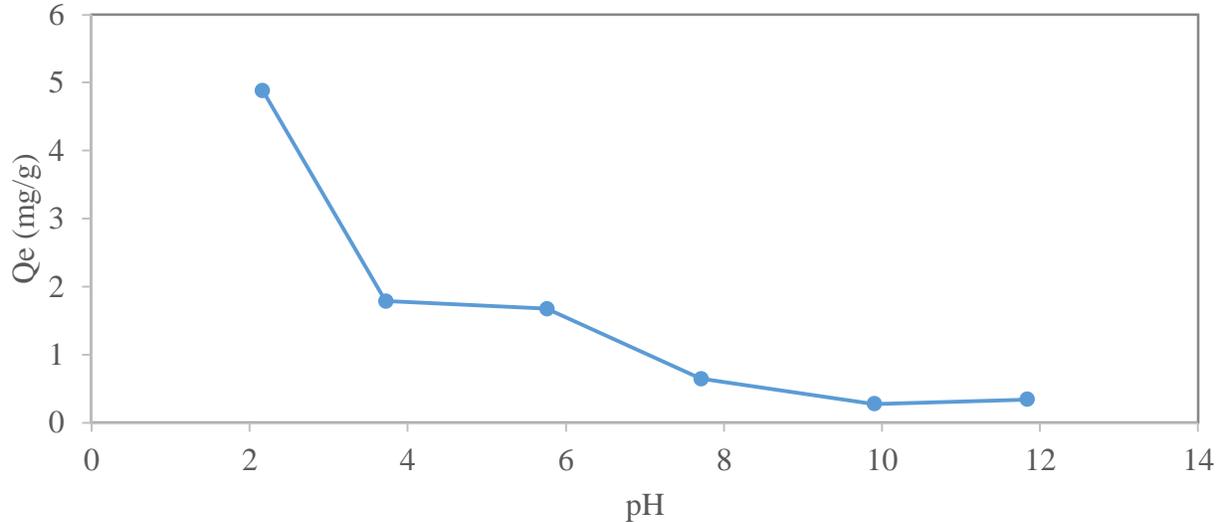


Figure 4.1.3: Effect of pH on gold (III) chloride adsorption onto activated carbon

4.2.3 Effect of adsorbent dosage on the adsorption of gold (III) chloride

The increase in adsorbent dosage reduces the adsorption capacity (q_e) as shown in Figure 4.1.4. According to Rodrigues et al [76] the amount of the adsorption sites decreases in the higher adsorbent dose due to the aggregation or overlapping of the adsorption sites. He asserts that it is associated to the adsorbent overcrowding and resulting in a lower q_e value. The highest Q_e was determined as 8.2837 mg/g at a dosage of 1.00 g/L attaining a percentage removal of 97.4%.

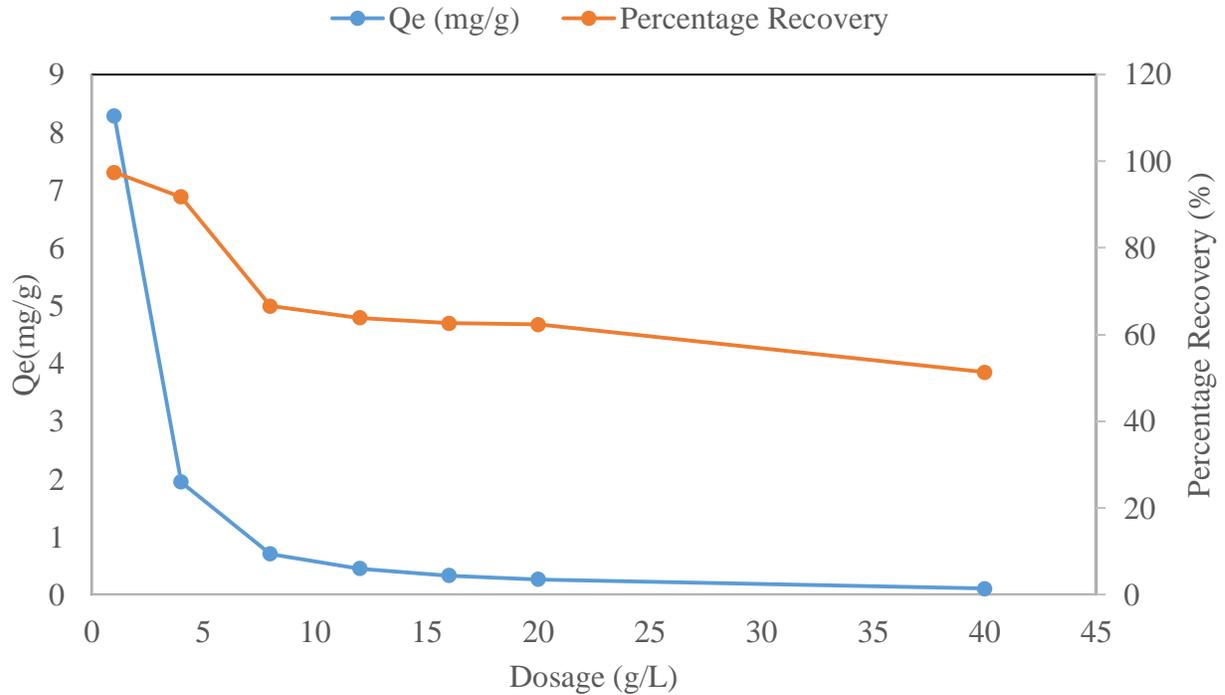


Figure 4.1.4: Effect of adsorbent dosage on the adsorption of gold (III) chloride

4.2.4 Effect of contact time on the adsorption of gold (III) chloride

As shown in Figure 4.1.5, the adsorption capacity for gold increased with increase in contact time. There was a sharp increase in the rate of adsorption for the first 200 minutes because the initial gradient between the adsorbate and the number of vacant sites available on the BDSAC surface was high. After 200 min there was a limited number of vacant sites and thus the mass transfer of the adsorbate molecules from the bulk liquid to the external surface reduced until after 6 hrs when the adsorption capacity was 4.69 mg/g.

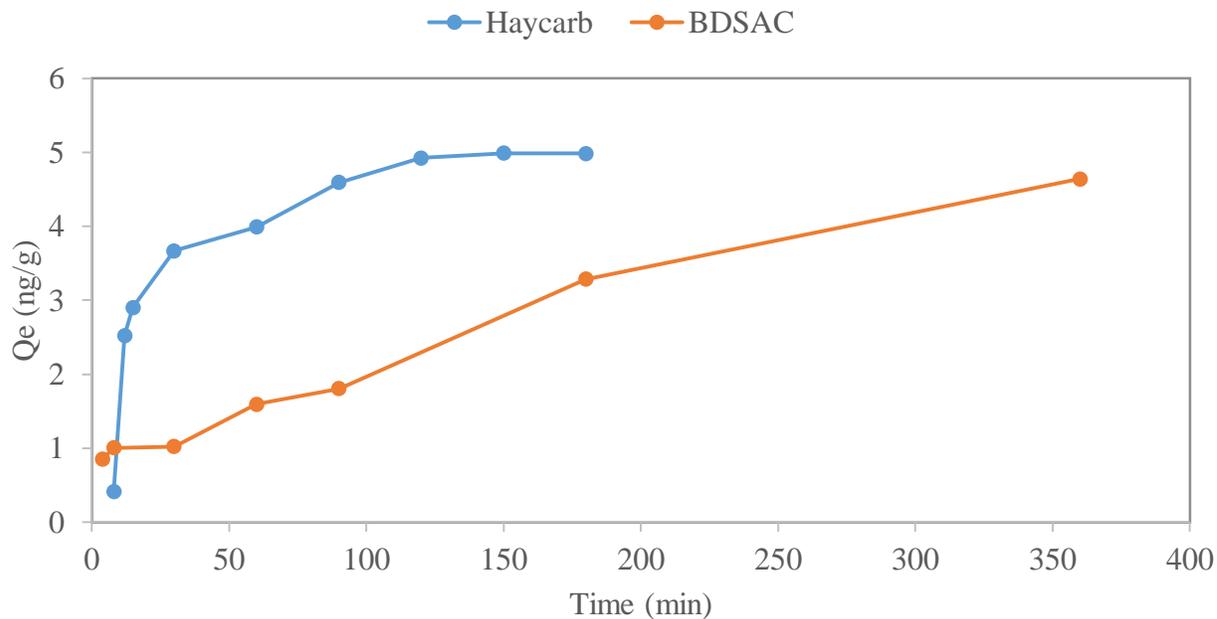


Figure 4.1.5: Effect of contact time on the adsorption of gold (III) chloride on BDSAC and Haycarb carbon

Haycarb carbon had a faster adsorption rate as shown in Figure 7. The rate of gold sorption increased rapidly for the first 30 minutes and reached equilibrium after 150 min. The rate is significantly greater than that of BDSAC because it could not reach equilibrium after 360 min.

4.2.5 Effect of temperature on the adsorption of gold (III) chloride

Increasing the temperature reduced the adsorption capacity of the BDSAC and this is explained by Mohan et al [77] as a phenomenon caused by the reaction being exothermic therefore the increase in temperature would favor the backward reaction. The increase in adsorption capacity of the adsorbent at 30 °C from 25 °C is due to the increase in reaction kinetics with temperature.

The optimum temperature for the adsorption of gold (III) chloride was determined as 30 °C before which the reaction is endothermic as shown in Figure 4.1.6.

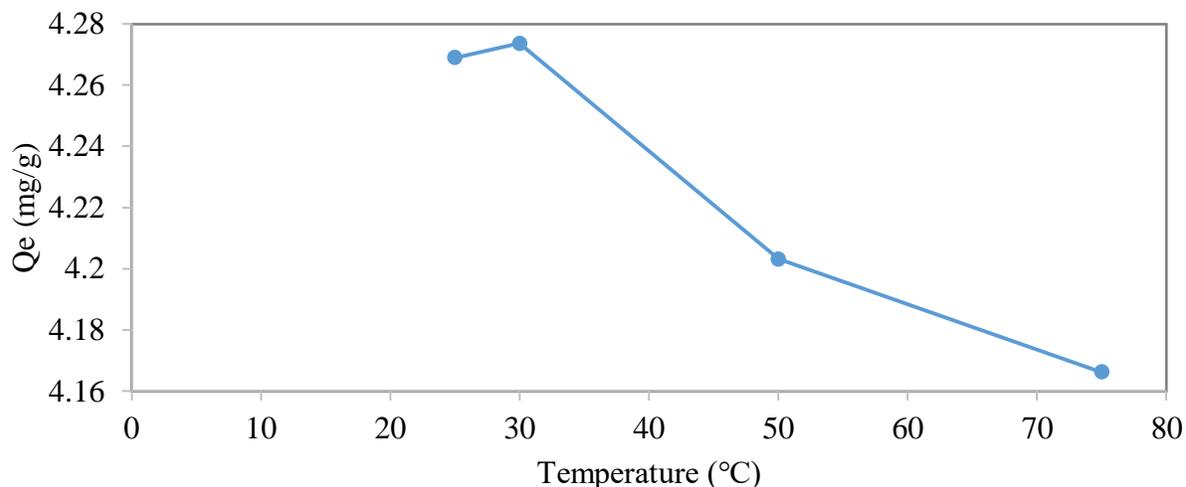


Figure 4.1.6: Effect of temperature on the adsorption of gold (III) chloride

4.2.6 Effect of ionic strength on the adsorption of gold (III) chloride

The change in ionic strength had no significant effect on the adsorption of gold (III) chloride onto the BDSAC as illustrated by Figure 4.1.7. This can be attributed to formation of an inner-sphere complex because the effect of ionic strength is used as a macroscopic method to distinguish inner from outer-sphere complexes [51]. It also implies that the ion bonds to a specific site on the surface thus ignores overall electrostatic interaction with the bulk surface.

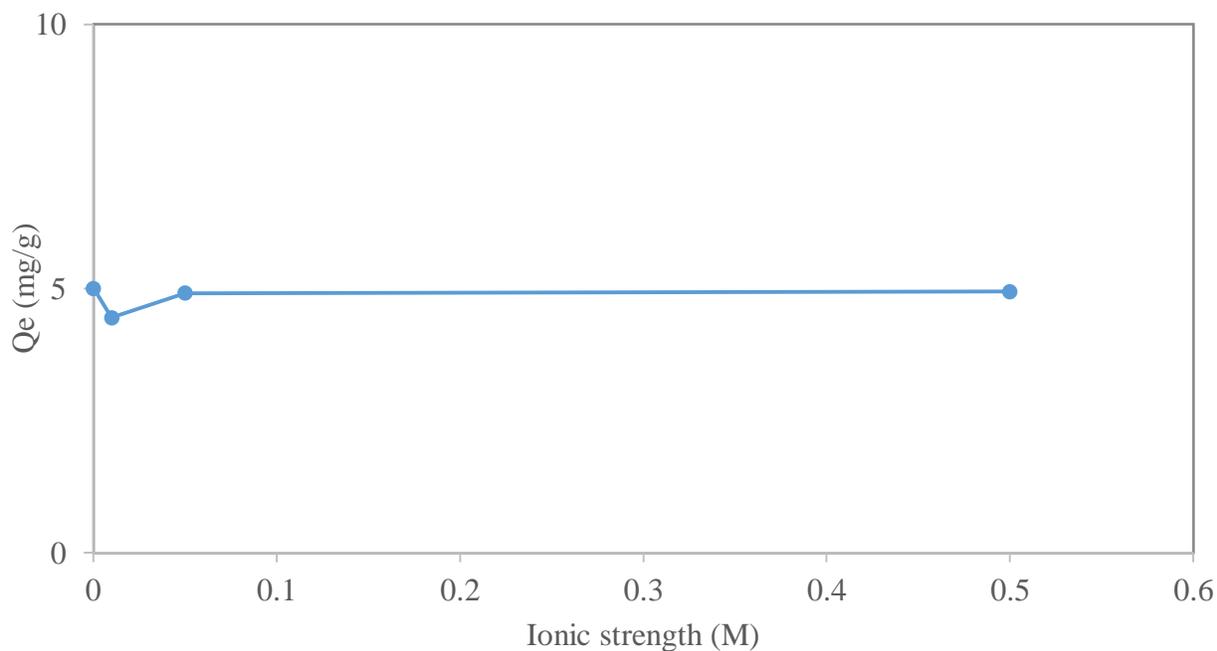


Figure 4.1.7: Effect of ionic strength on the adsorption of gold (III) chloride

4.2.7 Effect of initial gold(II) concentration on the adsorption of gold (III) chloride

As the initial gold concentration increased there was linear increase in the q_e value for BDSAC as shown in Figure 4.1.8. This is so because the adsorption capacity increased with increase in initial concentration. This phenomenon is in agreement with literature [50]. It is so because as the initial concentration increased, the strength of the driving force for the mass transfer was increased too and hence became favorable for the adsorption of the Au^{3+} ion [34]. In the case of Haycarb, the increase in initial gold concentration had no influence on the equilibrium concentration.

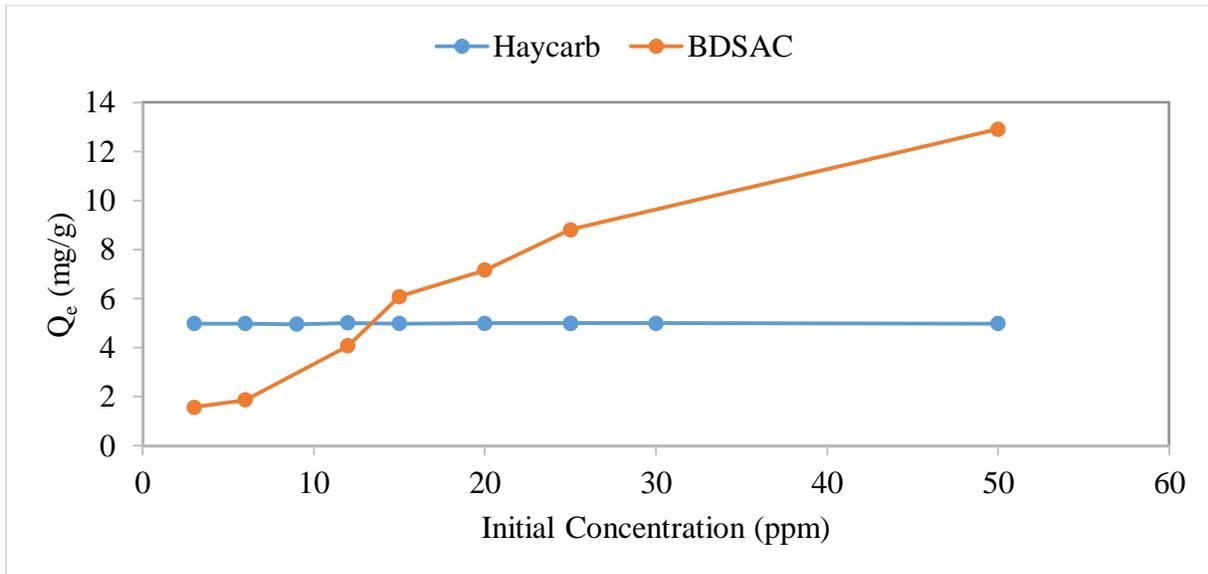


Figure 4.1.8: Effect of initial concentration on gold adsorption onto Haycarb carbon

4.3 Adsorption isotherms of gold(III) ions into BDSAC

Adsorption isotherms describe the interaction of the sorbent with the sorbate. The equilibrium studies determine the nature of the mechanism of the adsorbate and adsorbent interactions through sorption parameters evaluation. The relationship between the adsorbed Au(III) chloride ions and the equilibrium was described by Langmuir, Freundlich, Temkin, Dubin-Rafushkevich and Halsey isotherms.

4.3.1 Linear Langmuir isotherm

It can be written as

$$\frac{C_e}{q_e} = \frac{1}{KQ_m} + \frac{C_e}{Q_m} \quad (22)$$

Where C_e is the metal equilibrium in liquid phase (mg/L), q_e is the metal equilibrium concentration in adsorbed phase (mg/g), Q_m and K are Langmuir constants representing the adsorption capacity (mg/g) and energy of adsorption respectively.

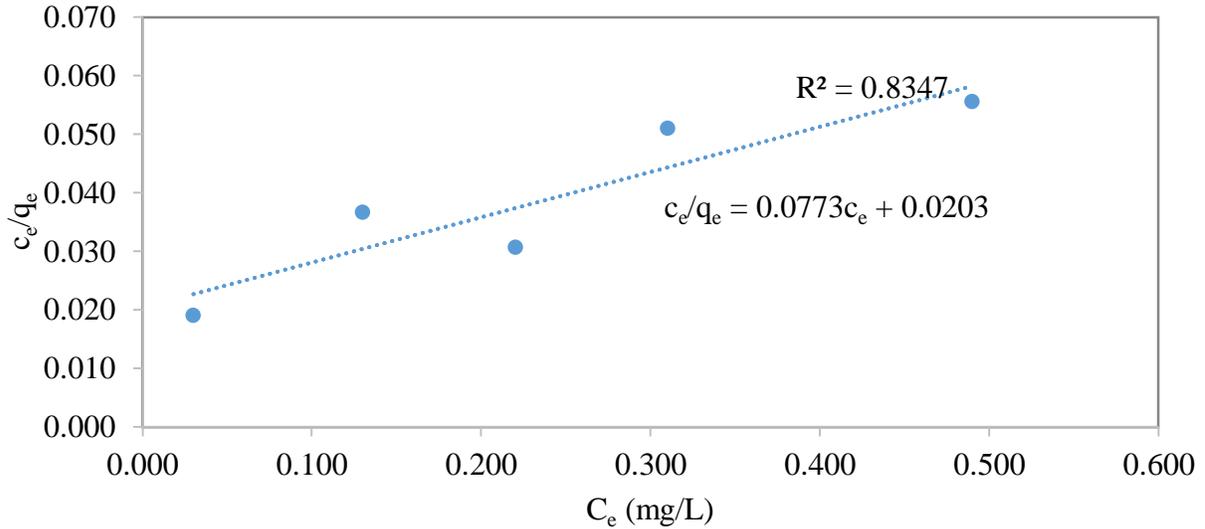


Figure 4.1.9: Linear Langmuir isotherm

The correlation coefficient using the Langmuir isotherm was determined as 0.8347 and the maximum adsorption capacity, Q_m was determined as 12.9366 mg/g from the graph shown in Figure 4.1.9. The value of the Langmuir constant was 3.8079 which is higher than that of Haycarb carbon at 3.42857. This implies that the adsorption process is homogenous and the energy of adsorption is very high compared to that of Haycarb activated carbon. The maximum adsorption capacity Q_m for the BDSAC was lower than that of Haycarb carbon (34.7222 mg/g) but it is higher than that of hard shell apricot stones at 6.028 mg/g at 25 °C [52].

The separation factor R_L which was derived using the equation below was used to determine the suitability of the BDSAC towards the Au^{3+} ions.

$$R_L = \frac{1}{1+KC_0} \quad (23)$$

Where K = Langmuir constant (L/mg), C_0 = initial concentration (mg/L)

All the R_L values for all concentrations were in the range $0 < R_L < 1$ indicating that the adsorption process was favorable.

4.3.2 Freundlich Isotherm

This model is represented by the following mathematical relationship

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (24)$$

Where Q_e is the amount adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg/L), n is the adsorption intensity (g/L) and, K_F is the adsorbent capacity (mg/g)(L/mg).

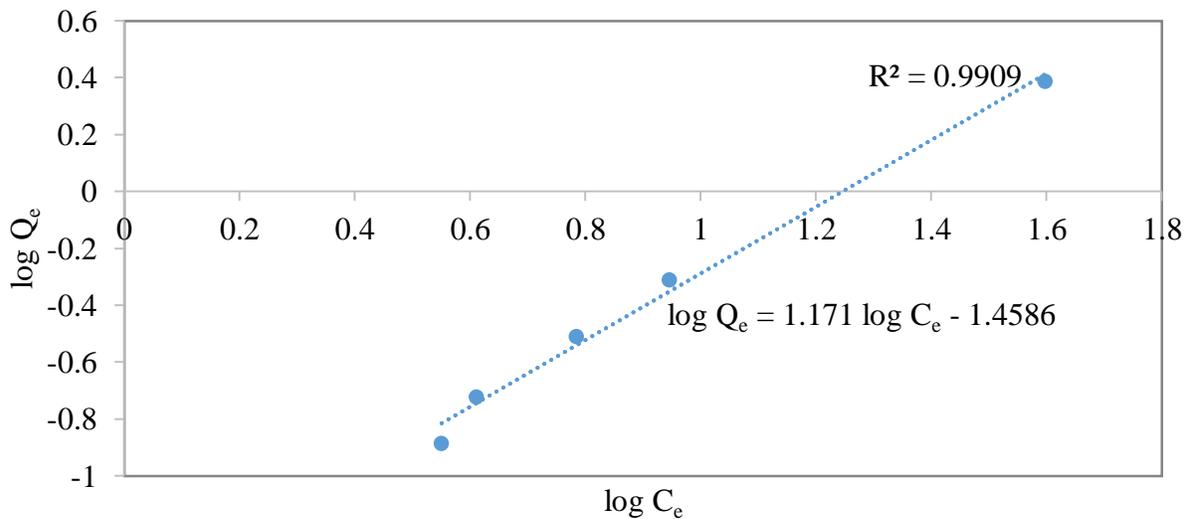


Figure 4.2.0: Linear Freundlich Isotherm

The correlation coefficient of the Freundlich isotherm ($R^2 = 0.9909$) shown in Figure 4.2.0 was higher than that of the Langmuir isotherm (0.8347) suggesting that the adsorption process is

better described by the Freundlich isotherm. The Freundlich isotherm describes the adsorption process as heterogeneous (multiple layer) adsorption due to the diversity of adsorption sites with uniform energy and is valid for multilayer coverage on adsorbate surface. The correlation coefficient was very high at 0.9909. The value of n, the adsorption intensity parameter, was 0.8540 g/L which is less than 1 thus the adsorption process is chemical adsorption [58]. The value for K_F was determined as 0.0347 mg/g denoting the affinity of the BDSAC for Au^{3+} .

4.3.3 Temkin Isotherm

The adsorption isotherm assumes that the heat of adsorption of all the molecules in a layer would decrease linearly with coverage due to indirect adsorbate/biosorbent interactions. It also postulates biosorption as characterized by a uniform distribution of binding energies, up to some maximum binding energy. This model is given by a general mathematical relationship as shown below

$$Q_e = \frac{RT}{b_t} \ln K_T + \frac{RT}{b_t} \ln C_e \quad (25)$$

Where T = absolute temperature (298K), R = universal as constant (8.314 J mol⁻¹ K⁻¹), K_t =Equilibrium binding constant, b_t = constant related to the heat of sorption.

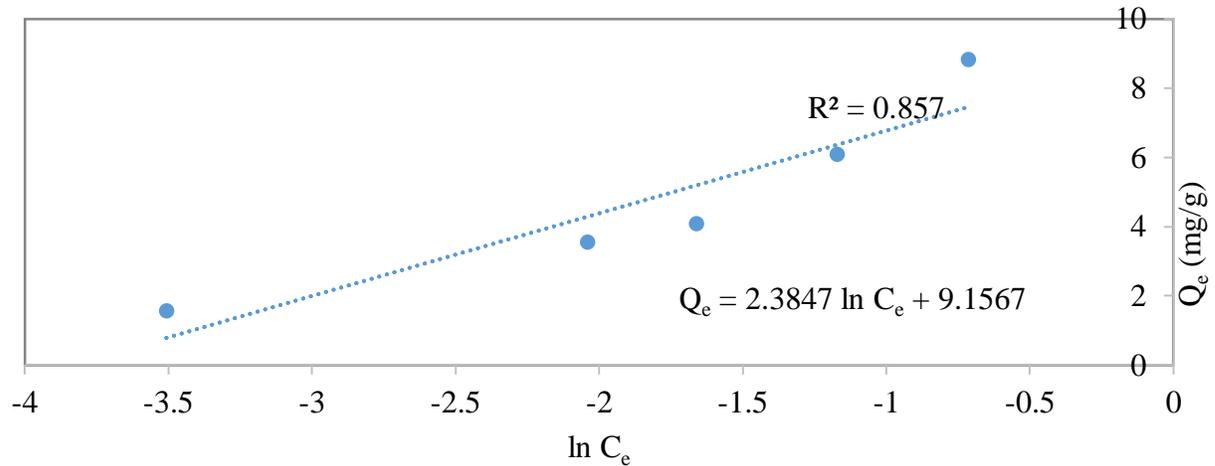


Figure 4.2.1: Linear Temkin Isotherm

The correlation coefficient was determined as 0.8570 from the graph in Figure 4.2.1 which is close to that of the Langmuir Isotherm and b_t was determined as 1 039.47 kJ/mol implying that the reaction is exothermic [23]. The value of K_t was 46.5148 L/g. The large values of the constants imply that there is a high BDSAC to Au^{3+} potential and there is a strong interaction between the sorbent and sorbate in the sorption mixture.

4.3.4 Dubinin –Radushkevich isotherm (D-R)

It estimates the apparent porosity and adsorption energy and its linear form can be expressed as [61]

$$\ln Q_e = \ln Q_m - \beta(RT \ln(1 + \frac{1}{C_e}))^2 \quad (26)$$

where Q_e = amount of Au^{3+} adsorbed at equilibrium, Q_D = adsorption capacity (mg/g), β = constant related to the adsorption energy, R = ideal gas constant, T = temperature in Kelvins, C_e = equilibrium concentration in mg/L

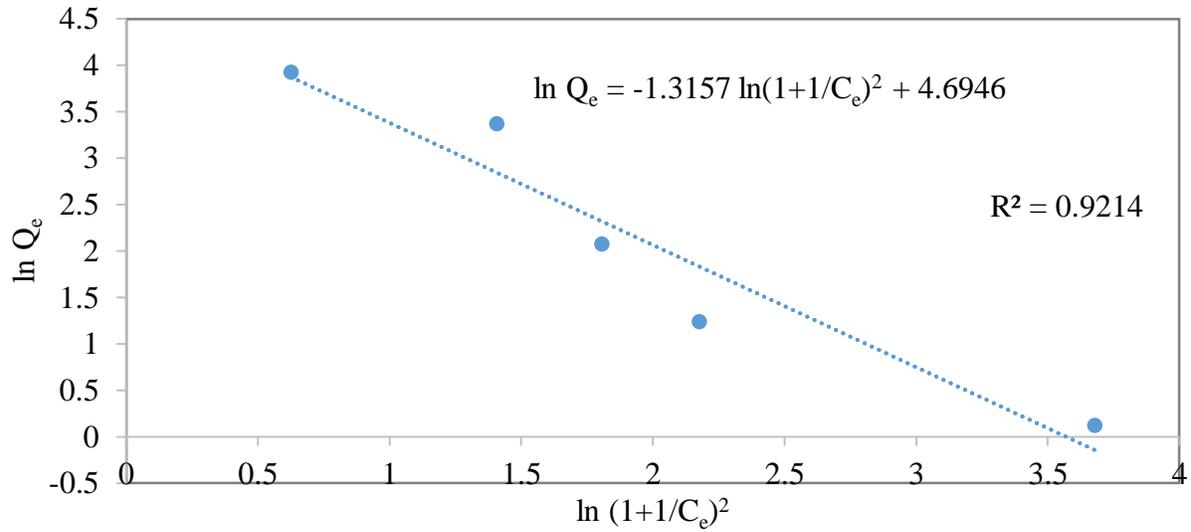


Figure 4.2.2: Dubinin –Radushkevich (D-R) isotherm

The value of β was determined as $2.1413 \times 10^{-7} \text{ mol}^2\text{kJ}^{-2}$ and the adsorption capacity, Q_D was 109.3551 mg/g. The correlation coefficient was 0.9214 from the graph shown in Figure 4.2.2.

This means that the adsorption process follows a pore filling mechanism.

4.3.5 Halsey adsorption isotherm

It predicts multilayer adsorption and fitting of equilibrium data to the model suggests the heteroporosity of the sorbent surface. It is represented in linear form as [59];

$$\ln Q_e = \frac{1}{n} \ln K_H - \frac{1}{n} \ln C_e \quad (27)$$

Where K_H and n = Halsey adsorption isotherm constants

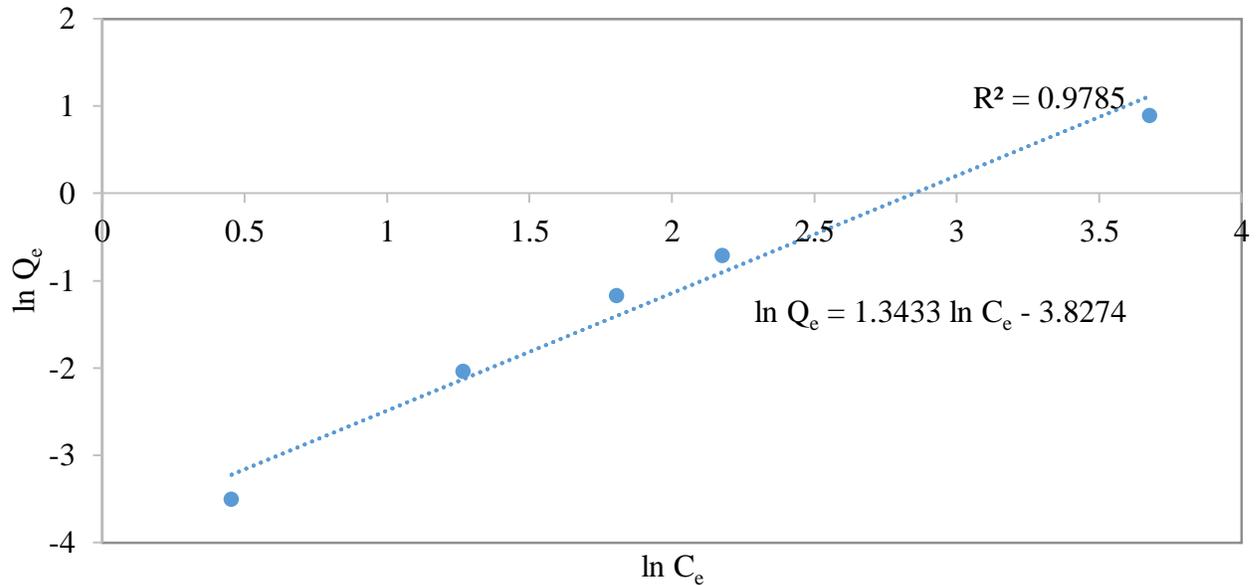


Figure 4.2.3: Halsey adsorption isotherm

The correlation coefficient was 0.9785 and the value of n was -0.7444. K_H was determined as 17.2749 using the equation shown in Figure 4.2.3.

4.4 Adsorption Kinetics

These are utilized in the investigation of the adsorption mechanism employing the pseudo-first order and pseudo-second order kinetic model.

4.4.1 Pseudo-first order kinetic model

The linear form of the equation is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (28)$$

Where q_e and q_t are Au^{3+} adsorption at equilibrium and time t and k_1 is the equilibrium time and adsorption rate constants (min^{-1})

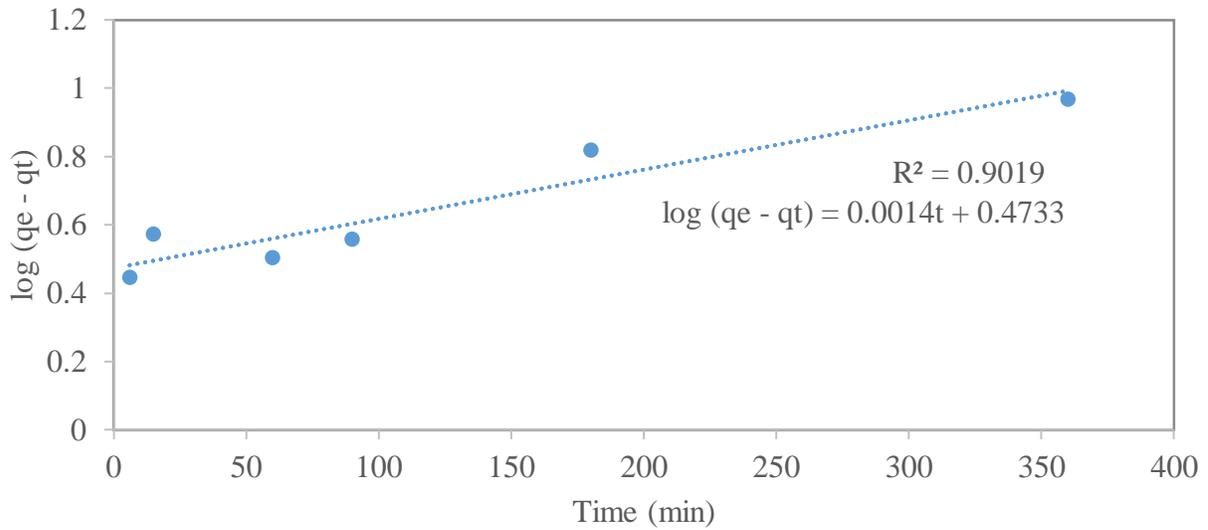


Figure 4.2.4: Pseudo-first order kinetic model

The constant for the pseudo- first order kinetic model was $-0.003224 \text{ min}^{-1}$ and q_e was 2.9737 mg/g . The correlation coefficient was determined as 0.9019 as shown in Figure 4.2.4. The q_e value for the pseudo-first order kinetic model is 2.9737 mg/g which is closer to the experimental q_e value of 5.00 mg/g .

4.1.2 Pseudo-second order kinetic model

It is expressed as shown below in its linear form

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1t}{q_e} \quad (29)$$

Where q_e and q_t are Au^{3+} adsorption at equilibrium and time t and k_2 is the adsorption rate constant for the Pseudo-second order kinetic model.

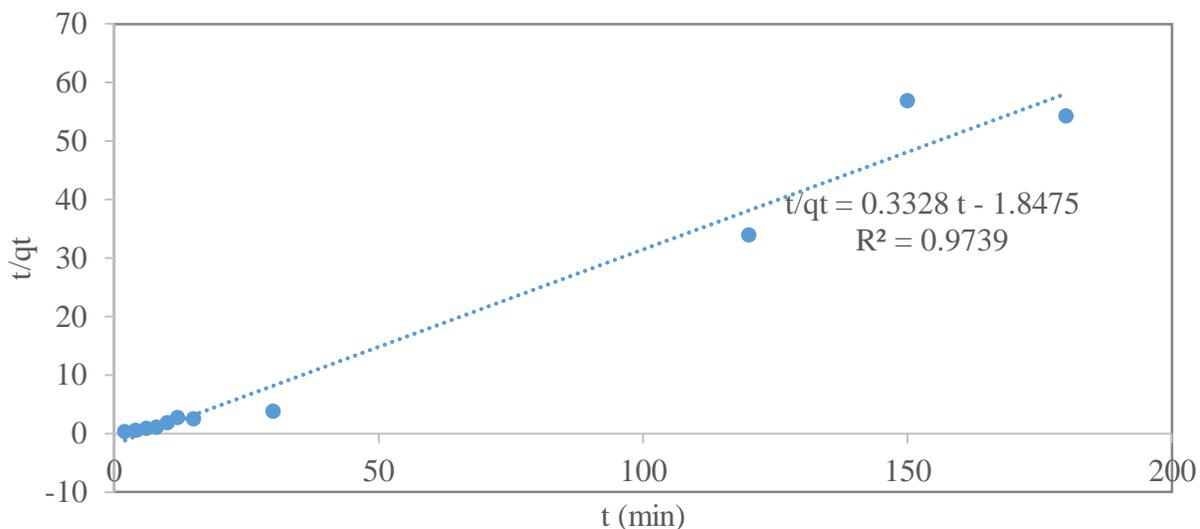


Figure 4.2.5: Pseudo-second order kinetic model

The equilibrium concentration was 3.0048 mg/g and k_2 was -0.0901. The correlation coefficient for the second-order kinetic model was 0.9739. The correlation coefficient, R^2 for the second-order kinetic model was significantly higher than that of the first-order kinetic model as shown in Figure 4.2.5. Moreover, the q_e value for the pseudo- second order kinetic model was 3.0048 mg/g which is closer to the experimental q_e . Thus it appeared that the system under study is more suitably described by the pseudo-second order kinetic model which is based on the assumption that the rate-limiting step may be sorption concerning valency forces through the sharing and exchange of electrons between the Au^{3+} ion and the BDSAC [78]. The rate-limiting step is a chemical reaction involving valence force changes through sharing or exchanging electrons between the adsorbate and adsorbent. The pseudo-second-order adsorption signifies the rate of

the adsorption is dependent on the availability of sorption sites on the sorbents rather than the concentration of the adsorbate in the bulk solution [79].

4.1.3 Spahn and Schlünder model

This model is chosen to describe the external diffusion on the adsorbent and its linear form is shown below

$$\ln \frac{C_1}{C_0} = -k_{ext}t \quad (30)$$

where K_{ext} is the external diffusion coefficient, C_1 is the concentration at time t

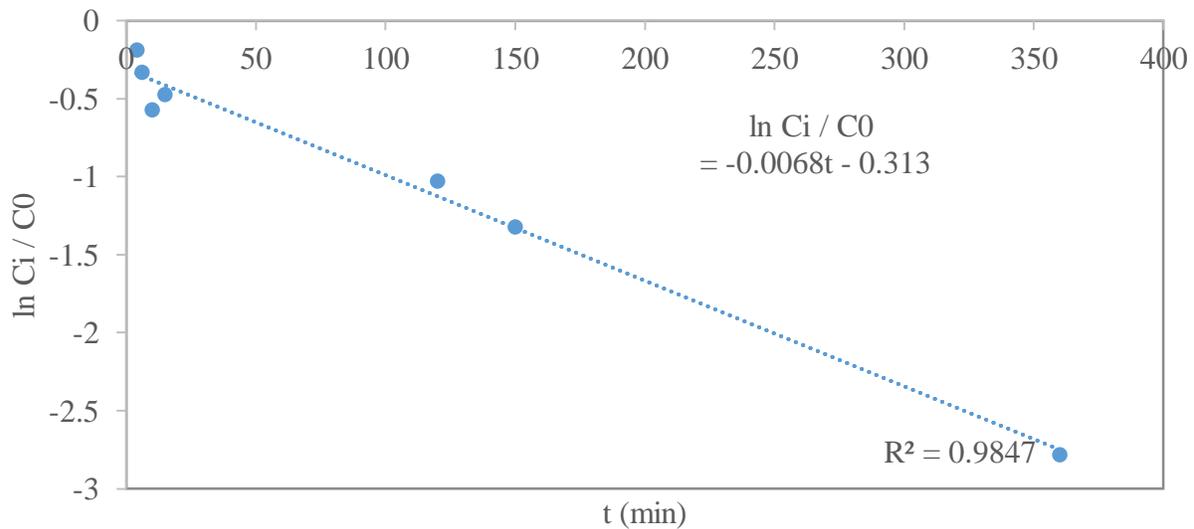


Figure 4.2.6: Spahn and Schlünder model

The value of the constant was 0.0068 and the correlation coefficient of the model, R^2 was determined as 0.9847 as shown in Figure 4.2.6 meaning that there was external diffusion during the sorption of Au^{3+} and it is the rate- limiting step.

4.1.4 Intra-particle diffusion model

This model shows if there is intra-particle diffusion of the Au^{3+} ions during adsorption and is expressed as shown below

$$q_i = k_p t^{1/2} + C \quad (31)$$

where k_p is the intra-particle diffusion rate constant, C is a constant related to the thickness of the boundary layer [59].

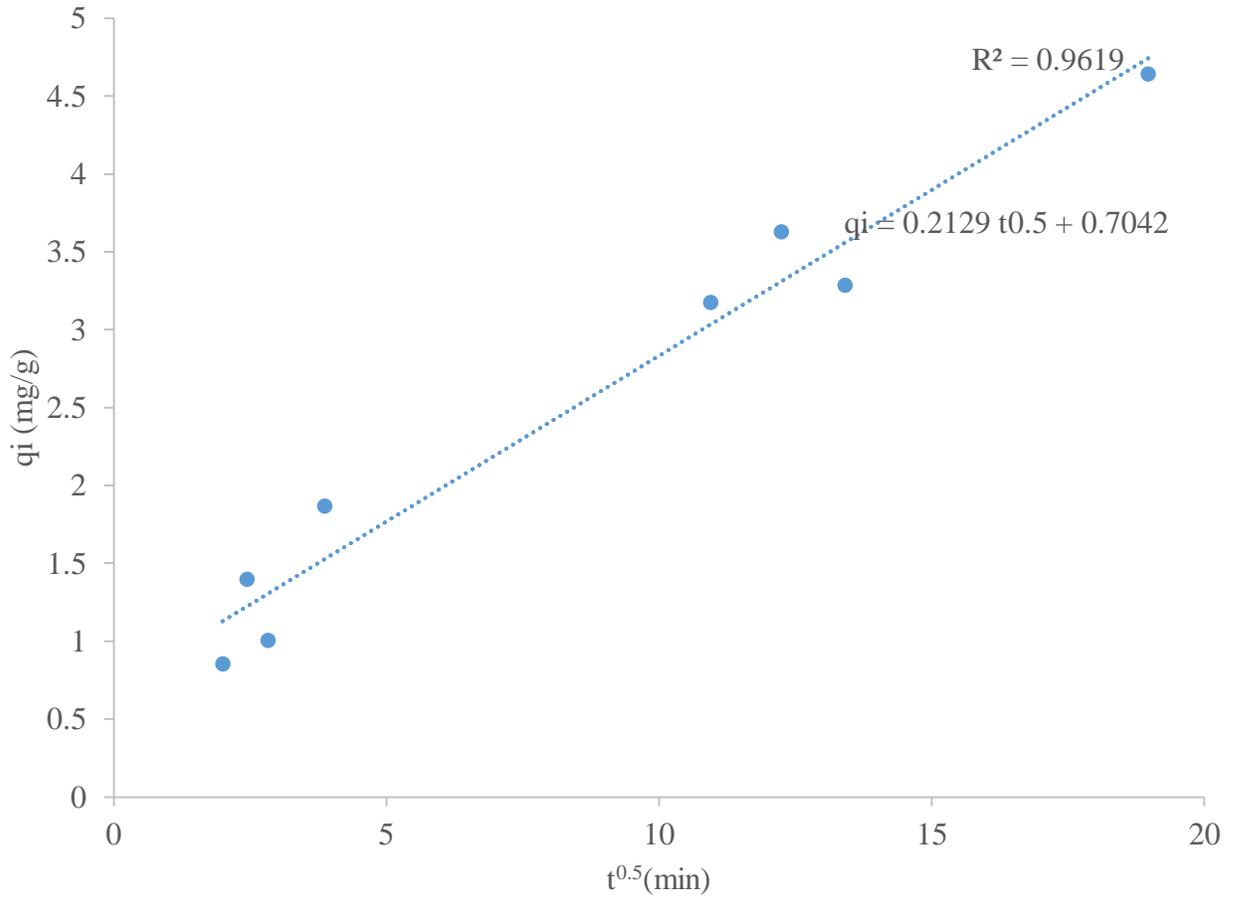


Figure 4.2.7: Intra-particle diffusion model

The graph for the intra-particle diffusion model is shown in Figure 4.2.7 above. The constant related to the thickness of the boundary layer was 0.7042 and the value of k_p was 0.2129. The plots of the model showed that the lines did not pass through the origin. This implied that the rate-limiting process was not only governed by the intra-particle diffusion but some other mechanism along with intra-particle diffusion was involved for the entire adsorption process [78].

The values in Table 4.1 show the sorption models and the parameters that were calculated after plotting the graphs.

Table 4.1: Sorption models with their respective parameters

MODEL	PARAMETER	BDSAC VALUE	HAYCARB VALUE
Langmuir	Qm (mg/g)	12.9366	34.7222
	R2	0.8347	0.9901
	K	3.8079	3.42857
Freundlich	KF (mg/g)(L/mg) ^{1/n}	0.0347	
	n (g/L)	0.854	
	R2	0.9909	
Temkin	Kt (L/g)	46.5148	
	bt (kJ/mol)	1 039.47	
	R2	0.857	
Dubinin–Radushkevich	β (mol ² kJ ⁻²)	2.1413×10^{-7}	
	QD (mg/g)	109.3551	
	R2	0.9214	
Halsey	R2	0.9785	
	N	-0.7444	
	KH	17.2749	
Kinetic Models			
Pseudo-first order	k1 (min ⁻¹)	-0.00322	
	qe (mg/g)	2.9737	5.00 SSD 134.619
	R2	0.9019	
Pseudo-second order	k2 (g/mg/min)	-0.0901	
	qe (mg/g)	3.0048	5.00 SSD 321.233
	R2	0.9739	
SPAHN AND SCHLÜNDER MODEL			
MODEL	Kext	0.0068	
	R2	0.9847	
INTRA-PARTICLE DIFFUSION MODEL			
MODEL	kp	0.2129	
	C	0.7042	
	R2	0.9619	

4.1.5 Comparison of BDSAC adsorptive capacities relative to studies done by others

This section focuses on comparing the results from this research to those done by others on the adsorption of gold from solution. The summary of the percentage recoveries of other adsorbents and the adsorbents used in this study are shown in Table 4.2.

Table 4.2: Percentage recovery comparisons between BDSAC and other adsorbents used by others

Precursor	% recovery	Ref
Furfuryl Thioalcohol	92.7	[36]
Hydrothermal Carbon spherules – monosacharride glucose	95	[79]
Hydrothermal Carbon spherules- disacharride sucrose	70	[79]
Hydrothermal Carbon spherules- polysacharride starch	62	[79]
Amberlite XAD-7HP resin	92.25	[10]
phosphonium-based ionic liquid (Cyphos IL 109)	99.4	[80]
Haycarb	100	This Study
BDSAC	100	This study

It is evident that BDSAC is a better adsorbent compared to other adsorbents used by other authors and its performance is comparable to that of Haycarb carbon.

Chapter 5

Conclusion and Recommendations

5.0 Introduction

This chapter focalizes on the findings from the project and their implications. It also provides the recommendations emanating from the project.

5.1 Conclusion

Activated carbon was successfully synthesized using H_2SO_4 and HNO_3 and exhibited the following functional groups as the as surface oxygen groups; hydroxyl, nitrate, amino, carboxyl, carbonyl and phenol groups. The biosorption of gold(III) chloride depends upon an optimum pH of 2.16, an optimized dosage of 0.002 g/L, contact time of more than 360 min, temperature of 30 °C, ionic strength of 0 M $NaNO_3$ and the adsorption capacity increases with the initial concentration of the gold solution. The optimum contact time for Haycarb was 150 min and the initial concentration had no effect on the adsorption of gold (III) ions.

The adsorption process was thus a chemisorption following a heterogeneous adsorption process. It was confirmed by the effect of temperature that the reaction is an exothermic reaction since as the temperature increased it caused a decrease in the Q_e value. The process was also confirmed to have a rate limited by external diffusion by the Spahn and Schlünder mode. This is the external diffusion of the gold ions from solution to the surface of the adsorbent on which it would be reduced.

From the experimental data, it is confirmed that the BDSAC can adsorb gold from solution and compared to Haycarb carbon it is only slower but the adsorptive capacities are the same. BDSAC competes not only with Haycarb for the adsorption of gold but with other precursors

5.2 Recommendations

- ✚ BDSAC should be employed in gold recovery because it was proven to adsorb gold significantly compared to other types of activated carbon.
- ✚ The desorption studies of gold adsorbed from chloride media by BDSAC should be investigated on.
- ✚ BDSAC can be employed in column sorption due the uniform particle size of the seeds after activation.
- ✚ BDSAC as a novel adsorbent can be utilized in other adsorption processes
- ✚ The regeneration of the BDSAC should be investigated on

References

- [1] Richard DA, Hiroyoshi N, Hajime K, Tsunekawa M. On the use of magnetite for gold recovery from chloride solution. Hokkaido University, 2013.
- [2] Zhang L, Li Z, Du X, Chang X. Activated carbon functionalized with 1-amino-2-naphthol-4-sulfonate as a selective solid-phase sorbent for the extraction of gold (III). *Microchim Acta* 2011;174:391–8. doi:10.1007/s00604-011-0643-y.
- [3] Morcali MH, Zeytuncu B, Ozlem E, Aktas S, Engineering M, Technology P, et al. Studies of Gold Adsorption from Chloride Media. *Mater Res* 2015;18:660–7.
- [4] Yazici E, Deveci H, Ehsani A. Recovery of metals from chloride leach solutions of waste of printed circuit boards by adsorption and precipitation. *Int. Miner. Process Congr.*, 2014, p. 170–9.
- [5] Zalupski PR, McDowell R, Dutech G. The Adsorption of Gold, Palladium, and Platinum from Acidic Chloride Solutions on Mesoporous Carbons. *Taylor Fr* 2014;32:37–41. doi:10.1080/07366299.2014.951278.
- [6] Salle JP. In-situ Adsorption of Gold (III) Chloride on Activated Carbon Under Pressure Oxidation-Leaching Conditions. McGill University, 2012.
- [7] Feng D, Provis JL, Deventer JSJ Van. Adsorption of gold on albite in acidic chloride media. *Hydrometallurgy* 2013;134–135:32–9. doi:10.1016/j.hydromet.2013.01.023.
- [8] Ran Y, Fu J, Rate AW, Gilkes RJ. Adsorption of Au(I, III) complexes on Fe, Mn oxides and humic acid. Elsevier B.V., 2002. doi:10.1515/chem-2015-0087.

- [9] Hastuti S, Kuncaka A, Nuryono. L-arginine-modified silica for adsorption of gold(III). *Indones J Chem* 2015;15:108–15.
- [10] Nguyen N Van, Lee J, Kim S, Jha MK, Chung K-S, Jeong J. Adsorption of gold(III) from waste rinse water of semiconductor manufacturing industries using Amberlite XAD-7HP resin. *Gold Bull* 2010;43:200–8. doi:10.1007/BF03214987.
- [11] Yaumi AL, Mustafa BG, Isah UA, Babagana G, Ojih FA. The effectiveness of coconut shell activated carbon on the adsorption of heavy metal using different activating agents . *Pharm Chem J* 2015;2:1–7.
- [12] Wankhade AA, Ganvir VN. Preparation of Low Cost Activated Carbon from Tea Waste using Sulphuric Acid as Activating Agent Abstract : *Int Res J Environ Sci* 2013;2:53–5.
- [13] Sahira J, Mandira A, Prasad PB, Ram PR. Effects of Activating Agents on the Activated Carbons Prepared from Lapsi Seed Stone. *Res J Chem Sci* 2013;3:19–24.
- [14] Pereira NC. Biomass and Bioenergy Production of bio-oil and activated carbon from sugarcane bagasse and molasses. *Biomass Bioenergy J* 2016;85:178–86. doi:10.1016/j.biombioe.2015.12.013.
- [15] Ahmad A, Ahmad A, Al-swaidan HM, Alghamdi AH. Production of Activated Carbon from Raw Date Palm Fronds by $ZnCl_2$ Activation. *JChemSocPak* 2015;37:1081–7.
- [16] Satayev MI, Alibekov RS, Satayeva LM, Baiysbay OP, Mutaliyeva BZ. Characteristics of Activated Carbons Prepared from Apricot Kernel Shells by Mechanical, Chemical and Thermal Activations. *Mod Appl Sci* 2015;9:104–19. doi:10.5539/mas.v9n6p104.
- [17] Sunil K, Jayant K. Adsorption for Phenol Removal-A Review. *Int J Sci Eng Res*

2013;1:2347–3878.

- [18] Mohan MA, Chadaga M. Methylene Blue Colour Removal Using Physically And Chemically Activated Cashew Nut Shell Activated Carbon. *Internantional J Technol Enhanc Emerg Eng Res* 2014;2:64–9.
- [19] Olivares-marín M, Fernández-gonzález C, Macías-garcía A, Gómez-serrano V. Journal of Analytical and Applied Pyrolysis Preparation of activated carbon from cherry stones by physical activation in air . Influence of the chemical carbonisation with H₂SO₄. *J Anal Appl Pyrolysis* 2012;94:131–7. doi:10.1016/j.jaap.2011.11.019.
- [20] Guo J, Xu WS, Chen YL, Lua AC. Adsorption of NH₃ onto activated carbon prepared from palm shells impregnated with H₂SO₄. *J Colloid Interface Sci* 2005;281:285–90. doi:10.1016/j.jcis.2004.08.101.
- [21] Das D, Samal DP, Bc M. Preparation of Activated Carbon from Green Coconut Shell and its Chemical Engineering & Process Technology. *J Chem Eng Process Technol* 2015;6. doi:10.4172/2157-7048.1000248.
- [22] Salarirad MM, Behnamfard A. The effect of flotation reagents on cyanidation ,loading capacity and sorption kinetics of gold onto activated carbon. *Hydrometallurgy* 2010;105:47–53. doi:10.1016/j.hydromet.2010.07.009.
- [23] Yang J, Qiu K. Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. *Chem Eng J* 2010;165:209–17. doi:10.1016/j.cej.2010.09.019.
- [24] Ruiz-Fernandez M, Alexandre-Franco M, Fernandez-Gonzalez C, Gomez-Serrano V.

- Development of activated carbon from vine shoots by physical and chemical activation methods. Some insight into activation mechanisms. *Adsorption* 2011;17:621–9.
doi:10.1007/s10450-011-9347-1.
- [25] Chen Z, Deng S, Wei H, Wang B, Huang J, Yu G. Activated carbons and amine-modified materials for carbon dioxide capture -- A review. *Front Environ Sci Eng* 2013;7:326–40.
doi:10.1007/s11783-013-0510-7.
- [26] Orwa C, Mutua A, Kindt R, Jamnadass R, Anthony S. *Agroforestry Database: a tree reference and selection guide*. vol. 4. 2009.
- [27] Soleimani M, Kaghazchi T. Activated Hard Shell of Apricot Stones : A Promising Adsorbent in Gold Recovery. *Chinese J Chem Eng* 2008;16:112–8.
- [28] Wills.B.A, Napier-Munn T. *Wills' Mineral Processing Technology*. 2006.
- [29] Syed S. Hydrometallurgy Recovery of gold from secondary sources — A review. *Hydrometallurgy* 2012;115–116:30–51. doi:10.1016/j.hydromet.2011.12.012.
- [30] Parajuli D. *Development of some novel lignin derivatives for adsorptive removal of heavy metals and recovery of precious metals*. Saga University, 2006.
- [31] Soleimani M, Kaghazchi T. Adsorption of gold ions from industrial wastewater using activated carbon derived from hard shell of apricot stones - An agricultural waste. *Bioresour Technol* 2008;99:5374–83. doi:10.1016/j.biortech.2007.11.021.
- [32] Wai W, Eugene L, Mujumdar AS. *Gold Extraction and Recovery Processes*. 2009.
- [33] Yu H, Zi F, Hu X, Nie Y, Xiang P, Xu J, et al. Adsorption of the gold-thiosulfate complex

- ion onto cupric ferrocyanide (CuFC)-impregnated activated carbon in aqueous solutions. *Hydrometallurgy* 2015;154:111–7. doi:10.1016/j.hydromet.2015.04.009.
- [34] Ahamed MEH, Mbianda XY, Bafubiandi AFM, Marjanovic L. Selective extraction of gold(III) from metal chloride mixtures using ethylenediamine- N-(2-(1-imidazolyl)ethyl)chitosan ion-imprinted polymer. *Hydrometallurgy* 2013:1–46. doi:10.1016/j.hydromet.2013.08.004.
- [35] Berdous D, Akretche DE. Recovery of Heavy Metal Using Solvent Impregnated Resin (SIR) Coupled with Donnan Dialysis 2012;2012:704–12.
- [36] Taylor P, Pan L, Wang F, Bao X, Pan L, Wang F, et al. Solvent Extraction of Gold(I) from Alkaline Cyanide Solution with Furfuryl Thioalcohol. *Sep Sci Technol* 2013:37–41. doi:10.1080/01496395.2013.783069.
- [37] Xu B, Yang Y, Li Q, Jiang T, Liu S, Li G. The development of an environmentally friendly leaching process of a high C, As and Sb bearing sulfide gold concentrate. *Miner Eng* 2016;89:138–47. doi:10.1016/j.mineng.2016.01.011.
- [38] Souza C, Majuste D, Dantas MSS, Ciminelli VST. Selective adsorption of gold over copper cyanocomplexes on activated carbon. *Hydrometallurgy* 2014;147–148:188–95. doi:10.1016/j.hydromet.2014.05.017.
- [39] Soleimani M, Kaghazchi T. The investigation of the potential of activated hard shell of apricot stones as gold adsorbents. *J Ind Eng Chem* 2008;14:28–37. doi:10.1016/j.jiec.2007.06.003.
- [40] House JOM and CL. *The Chemistry of Gold Extraction*. Second. Littleton, Colorado:

Society for Mining, Metallurgy, and Exploration, Inc; 2006.

- [41] Oghenejoboh K, Otuagoma S, Ohimor E. Application of Cassava Peels Activated Carbon in the Treatment of Oil Refinery Wastewater – a Comparative Analysis. *J Ecol Eng* 2016;17:52–8. doi:10.12911/22998993/62290.
- [42] Ngernyen Y, Tangsathitkulchai C, Tangsathitkulchai M. Porous properties of activated carbon produced from Eucalyptus and Wattle wood by carbon dioxide activation. *Korean J Chem Eng* 2006;23:1046–54. doi:10.1007/s11814-006-0028-9.
- [43] Vohra MS. Adsorption-Based Removal of Gas-Phase Benzene Using Granular Activated Carbon (GAC) Produced from Date Palm Pits. *Arab J Sci Eng* 2015;40:3007–17. doi:10.1007/s13369-015-1683-0.
- [44] Susheela P, Radha R. Production of activated carbon from dry coconut shell and its efficacy in treating waste water. *IJBS Res Pap* 2015;1:1–9.
- [45] Engineers C, Control D. Removal of Pb (II) ions from aqueous solutions by sulphuric acid-treated palm tree leaves 2015. doi:10.1016/j.jtice.2015.05.035.
- [46] Vargas DP, Giraldo L, Silvestre-Albero J, Moreno-Piraján JC. CO₂ adsorption on binderless activated carbon monoliths. *Adsorption* 2011;17:497–504. doi:10.1007/s10450-010-9309-z.
- [47] Valente Nabais JM, Canario T, Carrott PJ., Carrott RMM. Production of activated carbon cloth with controlled structure and porosity from a new precursor. *J Porous Mater* 2007;14:181–90. doi:10.1007/s10934-006-9023-0.
- [48] Zhao L.; Liu, D. X. W. Effect of several factors on peracetic acid pretreatment of

- sugarcane bagasse for enzymatic hydrolysis. *J Chem Technol Biotechnol* 2007;82:1115–21. doi:10.1002/jctb.
- [49] Chowdhury ZZ, Hamid SBA, Das R Das, Hasan MR, Zain SM, Khalid K, et al. Preparation of Carbonaceous Adsorbents from Lignocellulosic Biomass and Their Use in Removal of Contaminants from Aqueous Solution. *Bioresources* 2013;8:6523–55.
- [50] Wojnicki M, Paclawski K. Kinetics of the adsorption of gold(III) chloride complex ions onto activated carbon. *Arch Metall Mater* 2009;54:853–60.
- [51] Ramesh A, Hasegawa H, Sugimoto W, Maki T, Ueda K. Adsorption of gold (III), platinum (IV) and palladium (II) onto glycine modified crosslinked chitosan resin. *Bioresour Technol* 2008;99:3801–9. doi:10.1016/j.biortech.2007.07.008.
- [52] Soleimani M, Kaghazchi T. Recovery of Gold from Gold Plating Industry Wastewater Using an Agricultural Waste : Hard Shell of Apricot Stones. *Iran J Chem Eng* 2007;4:21–35.
- [53] Buah WK, Williams PT. Agricultural waste biomass converted to activated carbon as a material for gold processing. *J Mater Cycles Waste Manag* 2012;14:396–402. doi:10.1007/s10163-012-0083-8.
- [54] Buah WK, Williams PT. Granular activated carbons from palm nut shells for gold dicyanide adsorption. *Int J Miner Metall Mater* 2013;20:172–9. doi:10.1007/s12613-013-0710-y.
- [55] Nharingo T, Shoniwa V, Hunga O, Shumba M. Exploring the biosorption of Methylene Blue dye onto acid treated sugarcane bagasse. *Int J Curr Res* 2013;5:2169–75.

- [56] Wang S, Zhou S. Titania deposited on soft magnetic activated carbon as a magnetically separable photocatalyst with enhanced activity. *Appl Surf Sci* 2010;256:6191–8. doi:10.1016/j.apsusc.2010.03.139.
- [57] Yahorava V, Kotze M. Novel application of a gold cyanide selective resin in the PGMs industry. Randburg: 2003.
- [58] Dias NC, Steiner PA, Cristina M, Braga B. Characterization and Modification of a Clay Mineral Used in Adsorption Tests. *J Miner Mater Charact Eng* 2015;3:277–88.
- [59] Song C, Wu S, Cheng M, Tao P, Shao M, Gao G. Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation for Removal of Lead(II) From Aqueous Solutions 2014:86–98. doi:10.3390/su6010086.
- [60] He C, Hu X. Functionalized ordered mesoporous carbon for the adsorption of reactive dyes. *Adsorption* 2012;18:337–48. doi:10.1007/s10450-012-9410-6.
- [61] Maghsoudi M, Ghaedi M, Zinali A, Ghaedi AM, Habibi MH. Artificial neural network (ANN) method for modeling of sunset yellow dye adsorption using zinc oxide nanorods loaded on activated carbon: Kinetic and isotherm study. *Spectrochim Acta - Part A Mol Biomol Spectrosc* 2015;134:1–9. doi:10.1016/j.saa.2014.06.106.
- [62] Yacob AR, Wahab N, Suhaimi NH, Khairul M, Amat A. Microwave Induced Carbon from Waste Palm Kernel Shell Activated by Phosphoric Acid. *IACSIT Int J Eng Technol* 2013;5:2–5. doi:10.7763/IJET.2013.V5.545.
- [63] Karthikeyan S, Sivakumar P. The Effect of Activating Agents on the Activated Carbon Prepared from *Feronia limonia* (L .) Swingle (Wood Apple) Shell. *J Environ*

- Nanotechnol 2012;1:5–12. doi:10.13074/jent.2012.10.121009.
- [64] Shawabkeh RA. Synthesis and characterization of activated carbo-aluminosilicate material from oil shale 2004;75:107–14. doi:10.1016/j.micromeso.2004.07.020.
- [65] Ladhe U V, Patil PR. Removal of Yellow 2G dye from aqueous solutions using activated carbon prepared from mosambi and cotton an agricultural waste. IOSR J Environ Sci Toxicol Food Technol 2014;8:49–54.
- [66] Al-rawashdeh NAF. Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated palm tree leaves. J Taiwan Inst Chem Eng 2015;0:1–10. doi:10.1016/j.jtice.2015.05.035.
- [67] Bouchelkia N, Mouni L, Belkhiri L, Bouzaza A, Bollinger J-C, Madani K, et al. Removal of lead(II) from water using activated carbon developed from jujube stones, a low-cost sorbent. Sep Sci Technol 2016. doi:10.1080/01496395.2016.1178289.
- [68] Navarro P, Vargas C, Alonso M, Alguacil F. The adsorption of gold on activated carbon from thiosulfate-ammoniacal solutions. Gold Bull 2006;39:93–7. doi:10.1007/BF03215535.
- [69] Zhang J, Wang R, Cao X, Li Y. Preparation and Characterization of Activated Carbons from Peanut Shell and Rice Bran and a Comparative Study for Cr (VI) Removal from Aqueous Solution 2014. doi:10.1007/s11270-014-2032-8.
- [70] Vargas AMM, Cazetta AL, Garcia CA, Moraes JCG, Nogami EM, Lenzi E, et al. Preparation and characterization of activated carbon from a new raw lignocellulosic material : Flamboyant (Delonix regia) pods. J Environ Manage 2011;92:178–84.

doi:10.1016/j.jenvman.2010.09.013.

- [71] Jawad AH, Rashid RA, Ishak MAM, Wilson LD. Adsorption of methylene blue onto activated carbon developed from biomass waste by H₂SO₄ activation: kinetic, equilibrium and thermodynamic studies. *Desalin Water Treat* 2016;3994:1–13.
doi:10.1080/19443994.2016.1144534.
- [72] Lodeiro P, Sillanpaa M. Gold reduction in batch and column experiments using silica gel derivatives and seaweed biomass. *Chem Eng J* 2013;230:372–9.
doi:10.1016/j.cej.2013.06.105.
- [73] Shawabkeh R. Synthesis of activated carbon from spent lubricating oil and application for adsorption of cadmium and lead ions from aqueous solution. Mutah University, 2006.
- [74] Douadi A. Elimination of phosphorus by activated carbon prepared from algerian dates stones 2016.
- [75] Panneerselvam P, Morad N, Tan KA. Magnetic nanoparticle (F₃O₄) impregnated onto tea waste for the removal of nickel(II) from aqueous solution. *J Hazard Mater* 2011;186:160–8. doi:10.1016/j.jhazmat.2010.10.102.
- [76] Rodrigues LA, De Sousa Ribeiro LA, Thim GP, Ferreira RR, Alvarez-Mendez MO, Coutinho ADR. Activated carbon derived from macadamia nut shells: An effective adsorbent for phenol removal. *J Porous Mater* 2013;20:619–27. doi:10.1007/s10934-012-9635-5.
- [77] Mohan D, Sarswat A, Singh VK, Alexandre-Franco M, Pittman CU. Development of magnetic activated carbon from almond shells for trinitrophenol removal from water.

Chem Eng J 2011;172:1111–25. doi:10.1016/j.cej.2011.06.054.

- [78] Chowdhury ZZ, Zain SM, Khan RA, Islam MS. Preparation and characterizations of activated carbon from kenaf fiber for equilibrium adsorption studies of copper from wastewater. Korean J Chem Eng 2012;29:1187–95. doi:10.1007/s11814-011-0297-9.
- [79] Wang F, Zhao J, Zhu M, Yu J, Hu Y, Liu H. Selective adsorption – deposition of gold nanoparticles onto monodispersed hydrothermal carbon spherules : a reduction – deposition coupled. J Mater Chem A Mater Energy Sustain 2014;3:1666–74. doi:10.1039/C4TA05597G.
- [80] Nguyen VT, Lee J, Jeong J, Kim B, Chagnes A. Extraction of Gold (III) from Acidic Chloride Media Using Phosphonium-based Ionic Liquid as an Anion Exchanger. Ind Eng Chem Res 2015;54:1350–8. doi:10.1021/ie5045742.

Appendix

a) Apparatus

Crucible, volumetric flasks (50 mL, 100 mL, 500 mL, 1 000 mL and 2 000 mL), beakers (50 mL and 1 000 mL), burette (50 mL), conical flasks (250 mL), dropper, spatula, hammer, stirring rod, spatula, desiccator, pestle, mortar.

b) Reagents

Table A1: Reagents used

Chemical Name	Chemical Formular	Manufacturer	Mass/Conc
Gold Stock solution	H (AuCl ₄)	SMM Chemicals	1 000 ppm
Sodium Hydroxide	NaOH	Fizmerk	0.1 M
Nitric Acid	HNO ₃	ACE	15.8 M
Sulphuric Acid	H ₂ SO ₄	ACE	18.4 M
Sodium Hydrogen Carbonate	NaHCO ₃	Skylabs	0.1 N
Iodine	I ₂	Associated Chemical Enterprises	0.1 N
Sodium Thiosulphate	Na ₂ S ₂ O ₃	Saarchem	0.1 N
Sodium Nitrate	NaNO ₃	Glassworld	0.5 M

c) Instrumentation

Name	Model	Manufacturer	Use
Analytical balance	JJ224BC	G and G	weighing
Water bath shaker	ZWY-110X30	CE	shaking samples
FTIR Spectrometer	Nicolet 6700	Thermo scientific	identification of functional groups
pH meter	LE409	Mettler Toledo	determination of Ph
Magnetic stirrer			agitating solution
Oven	DHG-9070A		heating samples
FAAS	ice 3000	Thermo	identifying gold concentration

Appendix B**a) Serial dilutions from 1 000ppm stock solution**

The gold stock solutions of different concentrations were prepared in 50 mL volumetric flasks and topped to the mark with distilled water as shown in the table below

Table B1:Preparation of serial dilutions

Concentration (ppm)	Volume topped up to 50 ml volumetric flask
3	0.15
6	0.30
9	0.45
12	0.60
15	0.75
20	1.00
25	1.25
30	1.50
50	2.50
100	5.00

The 10 ppm solution was prepared in large quantities because it was employed throughout the study. For this solution, 20 ml from the stock solution of 1000 ppm was pipetted into a 2 000 cm³ volumetric flask which was topped up to the mark with distilled water.

Preparation of 1.0 M HCl solution

A volume of 98 ml was pipetted from the stock solution of 10.2 M (ACE Chemicals) into a 1 000 ml volumetric flask and topped to the mark with distilled water.

Preparation of 0.05 M HCl solution

A volume of 1.23 ml was pipetted from the stock solution of 10.2 M (ACE Chemicals) into a 250 ml volumetric flask which was topped to the mark using distilled water.

Preparation of 0.1 M HNO₃ solution

A volume of 1.58 ml was pipetted from a stock solution of 15.8 M (ACE Chemicals) into a 250 ml volumetric flask and distilled water was used to top the volume up to the mark.

Preparation of 0.01 M NaHCO₃ solution

A mass of 0.841 g NaHCO₃ granules (Skylabs) was added into a 1 000 cm³ volumetric flask and dissolved with distilled water and afterwards topped up to the mark with distilled water.

Preparation of 0.1 Na₂S₂O₃ solution

A mass of 6.2045 g of Na₂S₂O₃ (Saarchem) granules was dissolved in a 250 ml volumetric flask using distilled water and topped to the mark with distilled water thereafter.

Preparation of 0.1 M NaOH solution

A mass of 1 g of NaOH pellets (Fizmerk) was added into a 250 ml volumetric flask and dissolved using distilled water which was also used to top the solution to the mark.

Preparation of 1 M NaOH solution

A mass of 40 g was weighed and added into a 1 000 ml volumetric flask and dissolved using distilled water which was further used to top the solution to the mark.

Preparation of NaNO₃ solutions

The table below shows the masses of NaNO₃ (Glassworld) added into 50 ml volumetric flasks to prepare the concentrations indicated at the left side of the table.

Table B2:Preparation of NaNO₃ solutions

Concentration (M)	Mass added into 50 ml volumetric flask (g)
0.01	0.85
0.05	4.25
0.10	8.50
0.50	42.50

APPENDIX C

Results

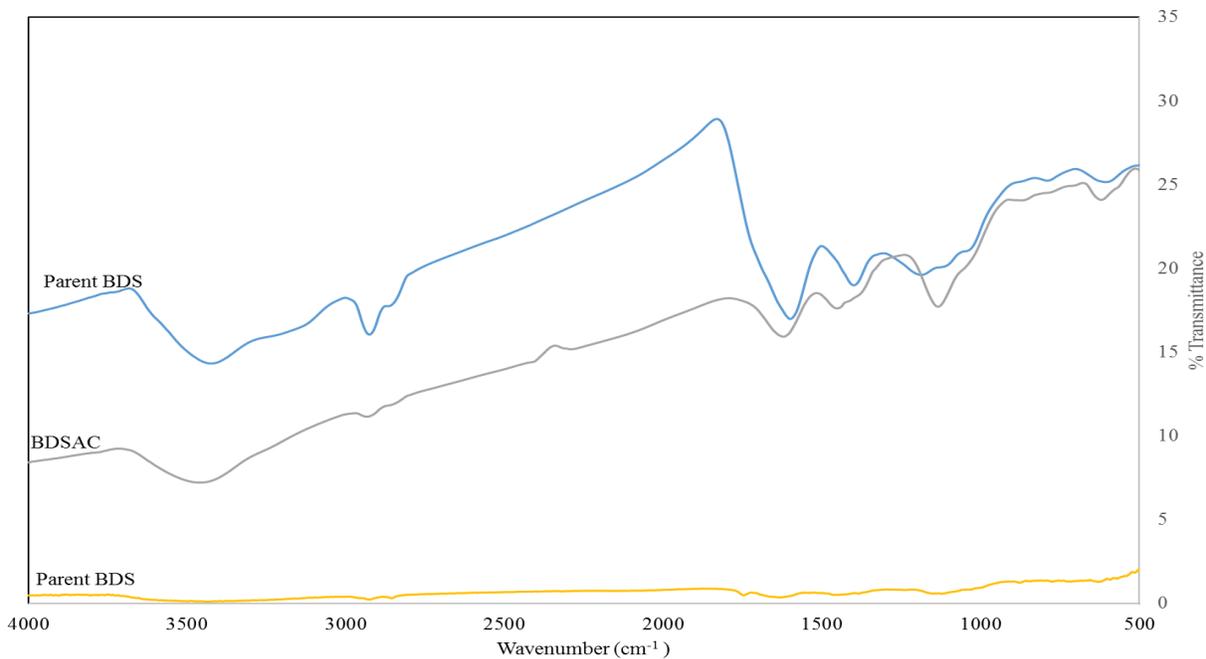


Figure C1: FTIR spectrum of (a) Parent / Raw BDS, (b) BDSAC and (c) BDSAC with adsorbed Au^{3+}

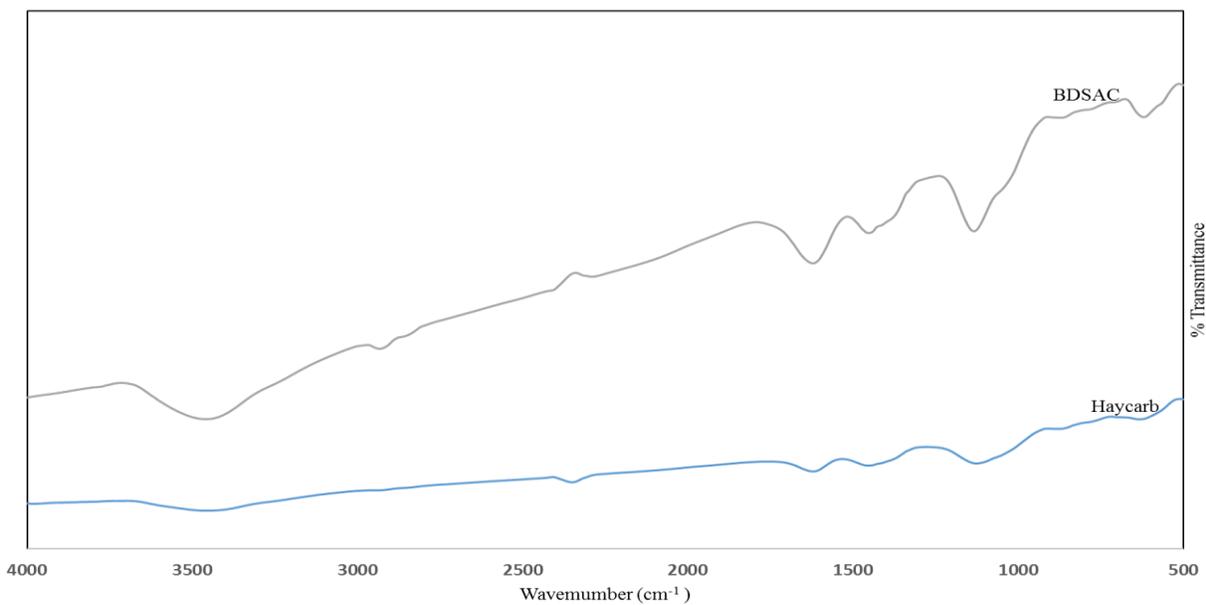


Figure C2: FTIR spectra of (a) BDSAC and (b) Haycarb carbon

