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Synthesis of corn cob activated carbon for Removal of free cyanide from geo-chemical laboratory effluent.

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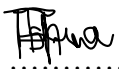
APPROVAL FORM

The undersigned parties confirm they supervised, read and endorse to the Bindura University of Science Education for the acceptance of a research dissertation entitled:

Synthesis of corn cob activated carbon for Removal of free cyanide from geo-chemical laboratory effluent.

Submitted by: ***Hlosimpilo Tshuma***

In partial fulfilment of the requirements for the Bachelor of Science Education Honors degree in Chemistry.



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DECLARATION FORM

I the undersigned, Hlosimpilo Tshuma, assert to the Bindura University of Science Education that this dissertation is my original work and all materials inclusive of academic sources added to my own has been recognized and cited. I also declare the current work has not been presented to any educational institution for merit purposes.

Signature……... Date……06/12/2024……

DEDICTIONS

The entire masterpiece is pledged to my proud father and mother as well as my siblings for their unseasoned love and support in me striving to become a chemistry teacher.

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I would also want to extend my appreciation to my academic mentor and supervisor Mr G Katengeza for his assistance and opinions in bringing this academic context to its best.

ABSTRACT

Ecologically safe, cost effective and efficient method suitable to meet up with governing regulatory standards of potable and manufacturing wastewater can be challenging. The current study gives a comprehensive analysis on lowering free cyanide concentration in wastewater by efforts to remove the compound using a low-cost corn cob activated adsorbent. The isolated wastewater bin was dosed successively with the active adsorbent after confirmations from pilot experiments to establish optimum conditions for the removal of the free cyanide compound, that is the effect of the dosage amount, pH and contact time. Scale up ratios were made on addition of the adsorbent to the bin, due to the increased waste water volume. Free cyanide wastewater was then treated with corn cob activated adsorbent at established conditions to remove the noxious compound. Optimal condition for free cyanide detoxification with the adsorbent were established at pH 6 and the final concentration of cyanide in the sample was measured to be 0.07 mg/L. The percentage removal of cyanide in the waste water was calculated to be 99%. Validation of cyanide analysis method using pyridine-barbituric reagent gives a linear regression equation with R^2 = 0.9998. The cyanide adsorption isotherms were described by the Langmuir model with regression R^2= 0.9549 and adsorption kinetics were fittingly described by the pseudo first-order model with regression R^2= 0.9251. The reaction was spontaneous and achievable. The most spontaneous reaction denoted by ΔG, was observed at 318 K which was -28.7542. The entropy (ΔS) for the detoxification experiment was 0.8608 J k^{-1} mol^{-1}.

ABBREVIATIONS

CCAA----------Corn Cob Activated Adsorbent

ICC----------Impregnated Corn Cob

APHA----------American Public Health Association

EMA----------Environment Management Agency

CN^- ----------Cyanide ion

rpm ---------- revolutions per minute

STP---------- Standard Temperature & Pressure

SOP---------- Standard Operating Procedure

WAD ---------- Weak Acid Dissociable

SAD ----------Strong Acid Dissociable

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Chapter 1 : INTRODUCTION

This chapter gives a background overview on the general chemistry, expected reactions associated with the use and chemistry of the cyanide.

1.0 Introduction

Cyanide a commonly used reagent in industries owing to its chelating capabilities and electrolytic functioning (Kuyucak, 2013). It also has been the favoured compound for the fore mentioned use, for a long period, because of its preferred cost, well proven chemistry, high stability of intermediate and product complexes and lastly its simplicity in recovery of gold after cyanidation with activated carbon (Marsden, 2006). These practices produce substantial quantities of cyanide waste.

Following gold reclamation, cyanide composites in gold mining deposit require treatment for the reason that, cyanide compounds are toxic to living organisms even at minute concentrations (Qiao Xiong, 2020). Environmental protection organisations around the globe have standardised particularly stringent regulations for drinking water with an allowable cyanide concentration of 0.2 mg/L or less (Qiao Xiong, 2020)

Biological (Sabatini, 2012) (Qiao Xiong, 2020), chemical, photochemical and adsorption means have been utilised to curb and detoxify cyanide compounds in wastewater so that they have concentrations that fall under regulations (Qiao Xiong, 2020). Alkaline chlorination also has been used to remove cyanide as well as iron/copper precipitation (Tyagi, 2018) hydrogen peroxide oxidation and UV/ozone oxidation are also have been looked into.

Even if these approaches have been verified to be effective in the research laboratories, numerous encounters, that is the high cost, low efficiency and harmful chemical reactions, has

imperfected extensive implementation of these approaches in manufacturing and industrial practices (Kuyucak, 2013). Consequently, an efficient and environmentally approachable process for treatment of cyanide compounds is a necessity.

(Qiao Xiong, 2020) informed, an adsorbent could upgrade and enhance the detoxification of cyanide in free cyanide-carrying wastewater by advancing instantaneous adsorption and degradation methods. The outcomes indicated that an activated adsorbent possibly will reduce the chemical methods, oxidants or chemical additives that can be used to detoxify free cyanide and enhance the elimination of cyanide. Other reports support and endorse activated carbon to eradicate cyanide from aqueous solution through adsorption (Agarwal, 2013;Singh, 2016;Aliprandini; 2020).

In spite of the finding, activated carbon is costly and is generally low in adsorption when matched with other carbon raw materials (Xiao, 2018). In consideration to contaminant adsorption, biochar is a prominent, effective and a budget sorbent material which can be employed in substitution of activated carbon (Chen, 2017; Dai, 2019). Nevertheless, biochar undoubtedly agglomerates as a result of charges on its own exterior groups and the intermolecular force of water (Qiao Xiong, 2020). The agglomeration impacts the effectiveness of the adsorption and detoxification of pollutants by biochar (Xiao, 2018).

This current work, describes a detailed study in which corn cob (Corn Cob Activated Adsorbent) biochar is employed to eliminate and detoxify free cyanide from a geo-chemical laboratory wastewater after leaching simulations for the recovery of gold by cyanidation (bottle roll). The adsorption measurements of the corn cob adsorbent, as well as the kinetics and isotherm of the cyanide removal method was attained (Qiao Xiong, 2020).

1.1 Problem statement

Industrial discharge tends to pose a major negative impact on the environment later the ecosystem at large. The discharge is hardly manageable to regulated discharge limits due to the constituent of highly toxic elements, for example, from geo-chemical assay laboratories, there are highest chances of containment of toxic cyanide from leach assay solution, heavy metals dissolved in solutions, acidic and alkaline solutions from the processes of assaying the mineral ores of their precious metals. Productions that release cyanide containing waste are required to retain concentrations lower than 0.2 mg/L (Turkmen, 1998) to prevent death by cyanide-intoxication. Failure to suppress the harmful compounds discharge can lead to intoxications that kill both micro and macro-organisms hence the need to detoxify the active chemical compound. Cyanide even at low concentrations is very lethal hence the need to regulate its discharge at allowable and supressed concentrations (Kuyucak, 2013).

1.2 Problem justification

Efforts in abiding to environmental regulations to avoid heavy penalties and practising safety for all, safe and sound measures should be put in place to detoxify the noxious active chemical in the waste effluent before discharging it in sewers, water bodies or even the ground hence ensure safety of the surrounding environment. The expense of treating waste storage facilities is a substantial percentage adding to the operating costs, nevertheless, unlike other operating cost, retain no economic return to the organisation. However, waste management is of greater importance for regulatory and economic reasons, to select the correct process, and then improve the operating conditions to minimize the cost of operation as well as to dispose waste in an environmentally friendly way by discharging less toxic emission.

1.3 Aim:

To detoxify free cyanide in Geo-chemical lab wastewater by adsorption using low-cost corn cob activated adsorbent.

1.4 Specific Objectives:

1. To characterise the synthesized corn cob activated adsorbent (CCAA).
2. To determine the pH, contact time, temperature and adsorbent dosage effects on cyanide removal from the wastewater.
3. Describe adsorption data with Langmuir and Freundlich isotherms.
4. To determine the thermodynamic properties for the adsorption process.

1.5 Delimitations to Study

The aim and objectives of this study are centred and relate only to wastewater from geochemical laboratory test work or any related laboratory facilities on exploration samples from leach assaying (source of the cyanide waste). Leach assay is a cyanidation process used in determining leachable gold in gold containing ores.

Chapter 2 : LITERATURE REVIEW

The chapter gives detailing aspects in relation to free cyanide definition, free cyanide uses, potential dangers (toxicity), free cyanide detoxification methods, adsorption characterization of adsorbent and regulations set for free cyanide detoxification.

2.1 Background

Cyanide is an excellent leaching reagent for gold and silver extraction, nonetheless, also figured a lethal chemical that has highest of chances to result in ecological pollution complications (Trapp, 2003). Cyanide is verified as a toxic contaminant, conferring to the Environmental Protection Agency (EPA) effluent guidelines (Anon., 2015). Dealing with the waste to an ecologically tolerable condition is consequently essential to prevent apparent and ground water pollution, as well as contamination of the overall atmosphere and human beings (Ebbs, 2004).

Mining businesses that employ cyanide in their operations, are then mandated by the International Cyanide Management to retain the concentration of cyanide withdrawn from their facilities to the lowest possible pollutant level of 0.2 mg/L prior to discharge (Eisler, 2004). In Zimbabwe local authorities, Environmental Management Agency (E.M.A) has mandated effluent and solid waste disposal to be within 4 separate regulated limits namely, blue, green, yellow and red, with a corresponding cyanide concentration of ≤0.07mg/L, ≤0.1mg/L, ≤0.15mg/L and ≤0.3mg/L respectively. The Statutory Instrument 6 of 2007 Environmental Management (effluent and Solid Waste Disposal) regulations, 2007 gives the local Zimbabwean regulated and recommended insight on limits of discharge for cyanide effluent & solid wastewater disposal.

2.2 Cyanide Toxicity

Cyanide can exist as a composite compound in an organic and inorganic form and as solid, aqueous and gaseous species (Jordan, 2020). Cyanide can be categorized generally into three toxic states Weak-Acid Dissociable (WAD), Strong-Acid Dissociable (SAD) and free cyanide which is the most toxic form of cyanide (Kuyucak, 2013). WAD cyanide is cyanide complexed with metals such as nickel, copper, cadmium and zinc, whereas SAD cyanide is cyanide complexed with metals such as gold, silver, iron and cobalt. Wastewater effluents discarded into the tailing dams or natural water bodies from cyanidation activities with moderate concentration of cyanide pose risk to the environment and wildlife since animals have interaction these water source. (Donato et al., 2017).

2.3 Weak-Acid Dissociable (WAD)

Weak Acid Dissociable (WAD) Cyanide, is a defined cyanide group that go through dissociation and release free cyanide if refluxed in less acidic settings (pH 4.5-6) (Donato, 2016). WAD cyanide is determined analytically through weak acid distillation and analysis of liberated free cyanide (Kuyucak, 2013). Weak acid dissociable cyanide provides a conservative estimate of toxicity as it recovers both free cyanide and weak metal cyanide complexes.

2.4 Strong-Acid Dissociable (SAD)

SAD is a rationally well-defined expression referring to the total amount of all the inorganic chemical forms of cyanide that dissociate and discharge free cyanide once refluxed under strongly acidic state. Nevertheless, it must be distinguished that roughly some of the strong metal cyanide complexes, such as those of gold, cobalt and platinum, may not be fully restored during the total cyanide analytical procedure (Kuyucak, 2013).

2.5 Free cyanide (cyanide anion and hydrogen cyanide),

This is the most common form of cyanide and is known for extreme lethal effect on living beings. At a pH 7 or less in water, free cyanide is present totally as HCN. Above pH 11, free cyanide exists entirely as CN^-. Free cyanide is capable of dispersing as Hydrogen cyanide gas at room temperature also at a pH 6 (Kuyucak, 2013). Free cyanide is restored and determined using gas diffusion examination.

Cyanide is considered as a P-listed lethal waste hence exceedingly regulated in its discarding (Jordan, 2020). Any form of cyanide is highly toxic and can be considered as lethal when it enters the human body through inhalation, ingestion, and absorption (Jordan, 2020). In addition, marine ecologies are extremely sensitive to low concentrations of CN^- (0.01 mg/L and 0.15 mg/L for continued and critical exposure (Cosmos, et al., 2020).

Table 2.1:The Permitted Limit for Cyanide Utilisation. (Cosmos Anning, 2019)

Regulation Agent	Cyanide limit (mg/L)
World Health Organization (WHO)	**0.05**
United State Environmental Protection Agency (USEPA)	**0.200 in drinking water**
American Conference of Governmental Industrial Hygienists (ACGIH)	**>50 in tailings pond**
India Central Pollution Control Board (CPCB)	**4.7 ppm in air**
Mexico	**0.200**
Environmental Management Agency EMA(Zimbabwe)	**0.07**

2.6 Detoxification of cyanide

Natural procedures varying from the basis on volatilization, oxidation, precipitation to microbial decay were conventionally employed in the dealings of gold mine waste in tailing

ponds (Kuyucak, 2013). Later, the development was to more closely organized processes such as alkaline chlorination or oxidation by SO_2 + air or SO_2 + air +H_2O_2 (Combine Ox process) (Kuyucak, 2013)

2.7 Carbon Adsorbents (Adsorption properties)

Table 2.2:Carbon Adsorbents Adsorption properties

Adsorbent	Adsorption capacity (mg/L)	pH	Activating agent	Activation condition	Reference
Activated Carbon (Commercial)	124.3	3	H_3PO_4	-	(Khezami, 2005)
Activated Carbon from coconut tree sawdust	3.5	3	H_2SO_4	Activation at 80 °C for 12 hrs in hot air oven	(Selvi, 2001) (Makrigiann, 2015)
Activated carbon from olive bagasse	88.59	2	-	Pyrolysis at 500 °C/activation at 850 °C	(Demiral, 2008) (Makrigiann, 2015)
Activated carbon from waste tires	48.08	2	CO_2	Pyrolysis and activation at 900 °C for 2 hrs	(Hamadi N.K., 2001) (Makrigiann, 2015)

2.8 Synthesis of CCAA

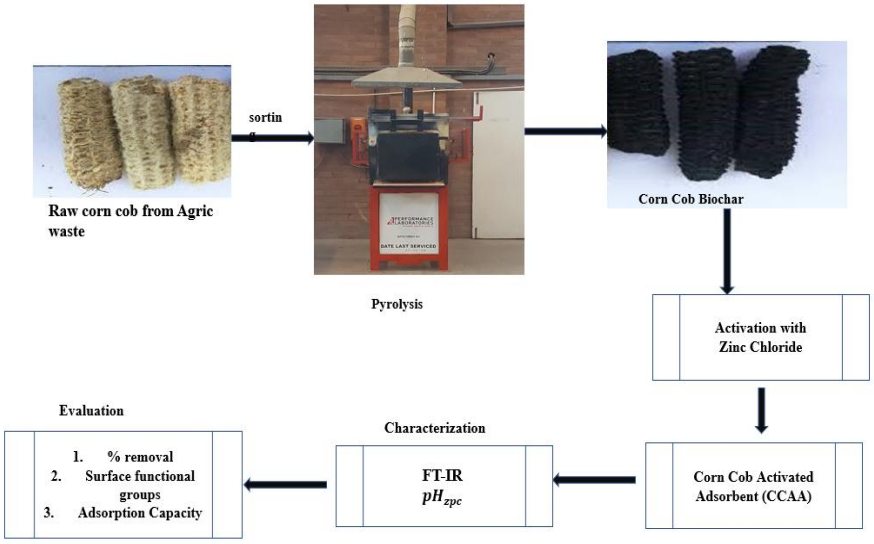

Fig 2.1:Process flow for CCAA synthesis, characterization and evaluation.

2.9 Carbon Activation

2.9.1 Physical Activation

Physical activation generally is executed at high temperature (500 to 1100 ^{o}C) by heating the material in an inert environment also called pyrolysis (Li, 2013).

2.9.2 Chemical Activation

Chemical activation done on agricultural or wooden raw material is done by impregnation with activating agent which degrades the cellulosic material within the material (Vassiliki Makrigianni, 2016). After impregnation in the absence of air, the material is heated, cooled, washed and dried. Zinc Chloride ($ZnCl_2$), Phosphoric acid (HPO_4) and Sulfuric Acid (H_2SO_4) are commonly used activating agent (Vassiliki Makrigianni, 2016).

2.9.3 Activated Carbon Structure

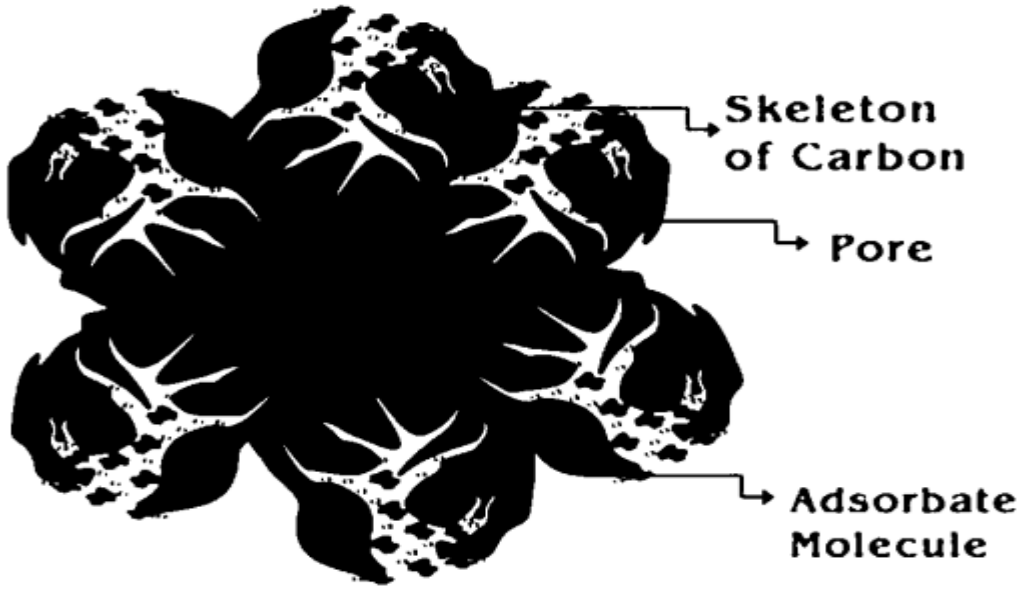

Fig 2.2: Activated Carbon Pores (Kan-Carbon Private Limited, 2015)

2.10 Adsorption Isotherm

The adsorption isotherm can be employed to measure or estimate the total CN^- ions eliminated and adsorbed by substances like corn cob activated adsorbents (CCAA). Sorption equilibrium is explained by the adsorption isotherms which are defined by persistent temperature equilibrium relation involving the equilibrium concentration of the adsorbate and the quantity of adsorbate adsorbed over a mass of the adsorbent (Khezami, 2005). Langmuir and Freundlich isotherms are generally used to estimate the adsorption features and behaviour (Vassiliki Makrigianni, 2016). For monolayer sorption, Langmuir isotherms are valid for surfaces with similar active sites related by equation expressed by equation 3.4. Freundlich isotherms verify adsorption onto different surfaces into numerous layers given by the expression equation 3.5 and equation *3.6* (Vassiliki Makrigianni, 2016).

Chapter 3 : MATERIALS AND METHODS

This chapter outlines the activities, methods and procedures carried out in the study, to attain solutions that address the objectives in determining factors that enhance use of corn cob activated adsorbent in detoxification of free cyanide in wastewater.

3.1 Equipment and Chemicals

All chemicals mentioned were analytical grades (AR), supplied from Merck and Sigma-Aldrich unless specified. The reagents were used without further purification. Amber reagent bottles were used to store prepared stock solutions to avoid disintegration by sunlight. All preparations were done in a fume hood to minimise exposure.

Table 3.1: Apparatus and Reagents

Apparatus	Reagents
pH meter Analytical Mass balance (LUNA) UV-Vis (PGI T60 190-1100 nm, China) magnetic stirrer electric muffle furnace drying oven boiler-reflux condenser thermometer stopwatch vacuum flask desiccator 50 ml Pipettes, 50 ml, 100 ml measuring cylinder	Potassium cyanide (KCN), 1 M Sodium hydroxide (NaOH), Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4.H_2O$), Pyridine-barbituric acid reagent 1 M Hydrochloric Acid (HCl) Chloramine-T solution (Sodium p-toluene-sulphonchloramide) Ferrous Sulphate ($FeSO_4$) 1 M Zinc Chloride ($ZnCl_2$) Distilled water

Whatman Filter Papers No. 1 mm x 252 cm Funnels, 10 ml, 50 ml, 100 ml, 1000 ml – Volumetric Flasks 200 ml, 500 ml beakers 1 ml(graduated), 10 ml, 50 ml Pipettes, 50 ml Burettes 250 ml Erlenmeyer Flasks	

3.1.2 Stock Solutions Preparation

a. Sodium Hydroxide 1 M

40 ± 0.1 g of sodium hydroxide pellets were dissolved in distilled water. The contents were allowed to cool and were then transferred to a 1-liter volumetric flask. The volumetric flask was then filled to the mark with distilled water.

b. Sodium Hydroxide 0.4 M

800 ml of solution in (a.) was measured and transferred to a 2-litre volumetric flask. It was filled to the mark with distilled water.

c. Sodium dihydrogen orthophosphate dihydrate 1.0 M buffer.

69 g of $NaH_2PO_4.H_2O$ was dissolved in a 100 ml of distilled water in a 500 ml volumetric flask. The contents were made to the mark with distilled water and refrigerated.

d. Pyridine-barbituric acid reagent

15 g of barbituric acid was placed in a 250 ml volumetric flask and 100 ml of was added to it, followed by 75 ml of pyridine. The mixture was mixed. Lastly 15 ml of

concentrated hydrochloric acid was added and mixed with the contents. The mixture was then cooled to room temp and diluted to the mark with distilled water.

e. Chloramine T

1.0 ± 0.01 g chloramine T was dissolved in 100 ml distilled water

f. Ferrous Sulphate

1.52 g of Ferrous Sulphate ($FeSO_4$) was added to 500 ml of distilled water to prepare 0.01 M $FeSO_4$

g. Calibration Standard Cyanide Stock Solution 100 mg/L

0.25 g of Potassium cyanide was dissolved in a 1000 ml volumetric flask with 0.4 M NaOH. The solution was made to the mark with the 0.4 M NaOH.

3.2 Sample Handling and Preparation

When the assay leach was complete and the samples analysed, the rejected solution and the analysed sample were discarded in an isolated 40 litres storage bin until it filled up. The bin was homogenised by mixing using a stirrer for approximately 2 to 3 minutes and for initial cyanide concentration determination, samples were taken from the isolated bin. A beaker was dipped in the solution to select a homogenised sample. On Whatman filter-paper, the selected sample solution was filtered to remove any suspended solid in the mixture as well as any other debris present in the sample. The standard operating procedure (SOP/CM16) (APHA, 2012) for cyanide determination in the wastewater was followed to determine the initial cyanide concentration on the UV-Vis (PGI T60, China**)** at a wavelength of 580 nm (Rodger Baird, 2017). Successive variations of the CCAA doses, pH variations and CCAA contact time with wastewater with the free cyanide, comparable to the commercial grade, $AC_{commercial}$, were made to the isolated bin as the experiments progressed to determine effect of the conditions to the free cyanide concentrations in the wastewater as well as assessing efficiency of CCAA versus

$AC_{commercial}$. This was carried down to monitor the detoxification behavior of the free cyanide and optimum conditions were established.

3.2.1 Working standard preparation (cyanide working standard 10 mg/L)

10 ml of cyanide prepared in step 3.1.2(g) was diluted to 100 ml volumetric flask by toping to the mark with 0.4 M NaOH. Serial dilutions were made from the produced solution to achieve the calibration standards. The solutions prepared were stable for 24 hrs and had to be prepared daily. Meant for the concentration determination on the UV-Vis (PGI T60, China**)** spectrophotometer the chemical test method, Determination of free cyanide by Spectrophotometry SOP/CM16 (APHA, 2012) effective from April 2022 was employed (Rodger Baird, 2017).

3.3 Corn cob adsorbent

Corn cobs were gathered from a local farm in Ruwa, Zimbabwe (Latitude: -17.8872 Longitude: 31.2402) and were washed with deionised water. The collected sample was oven dried at 110 ^{o}C for 1 hour, then pulverized to loosen the pith and chaff, followed by sieving using various sieves. Only the undersize of 250 microns were used. For each test 100 g of the undersize was made to mix with 250 ml of 1 M Zinc Chloride ($ZnCl_2$) solution. The impregnation was initiated at 363 K (90 ^{o}C) on a hot plate in a boiler-reflux condenser for 2 hours. the sample solution was filtered in a vacuum filter flask to collect the impregnated corn cob (ICC). The collected sample was oven dried overnight at 383 K (110 ^{o}C). The ICC was heated in an electric muffle furnace at a pyrolysis temperature of 773 K under a Nitrogen flow of about 300 cm^3/min STP. After pyrolysis the products were cooled, weighed and washed with hot hydrochloric acid followed by filtration in a vacuum flask. Further, the product was washed with hot distilled water to remove chlorides and other residues attached. Finally, the product was oven dried at 378 K (105 ^{o}C) for 6 hours. The resultant product was the corn cob activated adsorbent. The

method employed for the size distribution and pore volume were taken from Barrett-Joyner-Halenda (BJH) method (Vassiliki Makrigianni, 2016).

3.4.0 Adsorbent characterization

3.4.1 **FTIR characterization**

Functional groups existing on the adsorbent physical surface were observed on an FTIR Shimadzu IR Affinity-1 spectrometer (Kyoto, Japan) (Alves, 2013)running in the range 400 to 4000 cm^{-1} at a resolution of 4 cm. A spatula was used to add a pulverized sample of the CCAA to the crystal on the FTIR. The OMNIC Paradigm Software was used to record the spectral bands produced by the sample.

3.4.2 Determination of Moisture Content

5 samples of 2 g Corn Cob Activated Adsorbent (CCAA) samples were inserted in pre-heated crucibles. The crucibles were sealed and subjected to heat in an oven drier with confined air circulation for 2 hours at 110 °C (Donato, 2016). The samples were then placed in a desiccator and cooled to room temperature before proceeding to weighing.

Moisture content, M_c was computed by the equation:

$$M_C = (W_A - W_B - W_0)\ x\ 100\% \qquad 3.1$$

where**:**

M_C is the moisture content

W_A is the mass of crucible + sample before drying

W_B is the mass of crucible + dried sample

W_0 is the mass of crucible only

3.4.3 Point zero charge (pHpzc) determination

The pH displacement method was used to compute pHpzc. The CCAA was monitored its behaviour and results were taken at successive pH 2, 4, 6, 8, and 10. The pH of a 0.01M NaCl solution was changed to the desired pH by adding 0.01M hydrochloric acid or sodium hydroxide. A 2 g sample of CCAA was added to a 0.01M Alkaline solution in a conical flask, the pH was adjusted to 2, and

the mixture was homogenized and conserved at room temperature until 24 hours. pH of the sample mixture was recorded after filtering the conserved mixture. The data was used to plot a graph to calculate the pHpzc.

3.4.4 Adsorption

Adsorption studies were carried out on a magnetic stirrer at 150 rpm in a 250 Erlenmeyer flask, 2 g of CCAA was added to 100 ml of the waste water sample solution.

3.4.5.1 Effect of CCAA Dosage

Successive masses, 1 g, 2 g, 3 g, 5 g and 10 g of the CCAA was added to 100 ml of the waste water sample solution in an Erlenmeyer flask. Separate measurements were done for $AC_{commercial}$ and the contents were mixed at 150 rpm for 15 minutes. The mixture was filtered and the CN^- concentration was determined by the UV-Vis (PGI T60, China) spectrophotometer (Rodger Baird, 2017). The process was repeated and an average result was recorded as the final data obtained.

3.4.5.2 Effect of pH

The effect of pH on the rate of adsorption of the CCAA was evaluated by changing the parameter over the range 2 to 12. 100 ml of the 179 mg/L waste water sample solution was measured into an Erlenmeyer flask. The pH of the solution was varied from 2 to 12 using 0.01 M HCl or 0.01 M NaOH. 2g of CCAA was added to the flask containing the and the contents were stirred at 150 rpm for 15 minutes. The sample was filtered and analysed by the UV-Vis (PGI T60, China) spectrophotometer.

3.4.5.3 Effect of Temperature

Investigations on the effect of temperature were also examined in the process to optimize conditions for effective free cyanide detoxification by adsorption of the CCAA. 2 g of CCAA was added to a 100 ml waste water sample with the initial concentration of 179 mg/L, in an Erlenmeyer flask and was placed on a magnetic stirrer fitted with a hot element. The same procedure was repeated for $AC_{commercial}$. Temperature was regulated and varied in 5 ^{o}C margins from 25 ^{o}C to 55 ^{o}C. After successively running the process for 15 mins the sample was filtered and analysed by the UV-Vis (PGI T60, China) spectrophotometer. Using the *equation (3.2),* the percentage cyanide removed was computed.

3.5.1 Cyanide analysis

The cyanide concentration in the samples was analysed by the pyridine-barbituric acid method using Chloramine-T and was measured calorimetrically at 580 nm using a UV-Vis (PGI T60, China) spectrophotometer (APHA, 2012) (Qiao Xiong, 2020).

The cyanide removal percentage $CN_{\%}$ was calculated as follows:

$$CN_{\%} = \frac{C_i - C_f}{C_i} x\ 100 \qquad 3.2$$

Where:

$CN_{\%}$ is the cyanide removal percentage

C_i is the initial cyanide concentration

C_f is the final cyanide concentration

3.5.2 Adsorption capacity

$$Q_e = \frac{C_i - C_f}{m} \; x \; V \qquad 3.3$$

Where:

Q_e is the adsorption capacity

C_i is the initial cyanide concentration

C_f is the cyanide concentration at equilibrium

m is the mass of CCAA

V is volume of sample

3.5.3 Adsorption isotherms

Langmuir and Freundlich's isotherms were employed for description of the adsorption process of free cyanide using the equilibrium data (Vassiliki Makrigianni, 2016). The study of the isotherms was carried out at optimum pH by conducting batch experiments on a magnetic stirrer at 150 rpm in a 250 Erlenmeyer flask with 2 g of CCAA added to 100 ml of waste water sample solution, at period ranging 15 to 60 minutes. The experiment was first carried out at room temperature and then varied to check the behaviour at the corresponding temperatures.

For Langmuir isotherm the equation below was employed (Khezami, 2005):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_l} + \frac{C_e}{Q_m} \qquad 3.4$$

Where:

Q_e is the equilibrium adsorption capacity

C_e is the equilibrium concentration.

K_l is the Langmuir constant related to the binding sites

Q_m is the maximum adsorption capacity

For Freundlich isotherm, the below equation was employed:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad 3.5$$

$$log\ \ Q_e = log\ \ K_f + \frac{1}{n} log\ C_e \quad 3.6$$

Where:

Q_e is the equilibrium adsorption capacity

C_e is the equilibrium concentration.

K_f is the Freundlich constant related to the adsorption capacity.

$\frac{1}{n}$ is the Freundlich constant related to adsorption intensity.

3.5.4 Adsorption kinetics

3.5.4.1 First order pseudo kinetics equation

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \quad 3.7$$

Where:

q_e is the amount absorbed

q_t is the quantity absorbed at a specific time t

k_1 is the rate constant for the pseudo first order absorption

3.6.4.2 Second-order pseudo kinetic equation

$$\frac{t}{q_t} = \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e} \quad 3.8$$

Where:

q_e is the amount absorbed

q_t is the quantity absorbed at a specific time t

k_2 is the rate constant for the pseudo second order absorption

3.6.5 Thermodynamics

Thermodynamical features, enthalpy (ΔH), Gibbs free energy (ΔG), as well as entropy (ΔS) for the adsorption were calculated according to the following equations (Makrigiann, 2015):

$$\Delta G^0 = -RTlnK_L \quad 3.9$$

$$lnK_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad 3.10$$

$$\Delta G^0 = \Delta H^0 - T\Delta \quad 3.11$$

Where:

T denote absolute temperature in Kelvins (K),

R is the ideal gas constant

K_L is distribution coefficient.

The van't Hoff is employed in the evaluation of variations in equilibrium constants with temperature (Vassiliki Makrigianni, 2016). Enthalpy (ΔH^0) as well as entropy (ΔS^0) variations in the process were determined from the slope and intercept of the linear Van't Hoff plots in the graph $\ln K_L$ against 1/T.

Chapter 4 : RESULTS AND DISCUSSION

4.0 Results and Discussion

Introduction

The chapter briefs the outlook of the results that underlines the basis of the project. a full statistical analysis and mathematical modelling for the hypothesis of the project are outlined to validate all test made at the waste water analysed

4.1: Waste water analysis

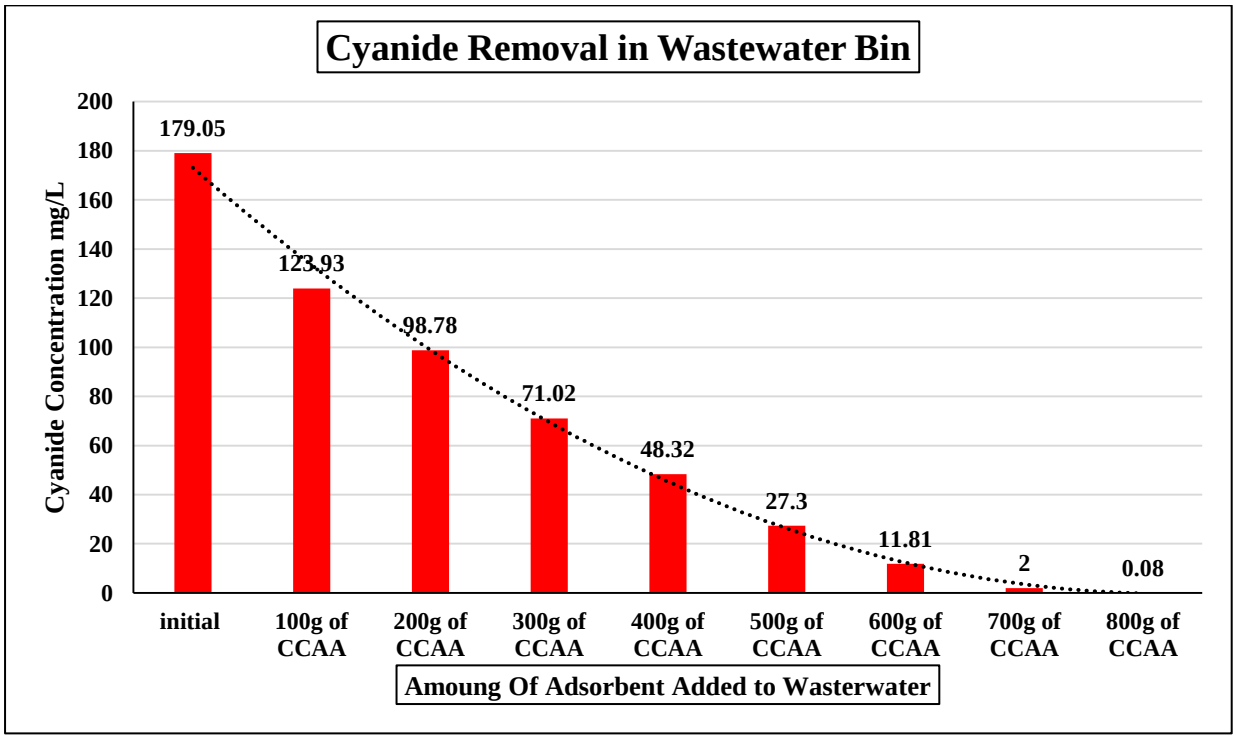

Fig 4.1: Cyanide Removal in Wastewater Bin

Fig 4.1 shows the analysis of cyanide concentrations in the isolated waste water bin. In the initial analysis on the wastewater sample using SOP/CM16 (APHA, 2012) with UV-Vis finish analysis. The highest recorded concentration of free cyanide was found to be 179 mg/L. The concentration was determined at an alkaline state of the waste water since the cyanidation assay favor alkaline conditions. Successive variations were made to the isolated bin to monitor the

detoxification behavior of the free cyanide and optimum conditions were established. The pH was corrected to a pH of 6, also 100 g of the CCAA were successively added to the bin for in 12 hours intervals for a period of 96 hours and the conditions made a resultant marginal difference between the initial free cyanide concentration at 179 mg/L to a final concentration at 0.07 mg/L, a permissible concentration. The same conditions were established for 800 g of $AC_{commercial}$ dose which had a seemingly identical result in which the initial 179 mg/L of the initial concentration was lowered to 0.08 mg/L. From the result, the percentage removal of cyanide in the waste water was calculated to be 99%. (Manyuchi, et al., 2022) reported a 75% efficiency of cyanide removal in gold mining wastewater using biochar, however the efficiency was lowered by presence of other cations in the wastewater.

4.2. Synthesized CCAA and $AC_{commercial}$

Fig 4.2:Synthesized CCAA and ACcommercial

4.2.1 Characterization of the Corn Cob Activated Adsorbent

Table 4.1 The physical properties of CCAA with activation and $AC_{commercial}$.

Sample ID	Pyrolysis temp (K)	Time (Hrs)	Impregnation ratio (% wt.)	Total pore volume (cm^3/g)
$CCAA_1$	773	1.0	100	0.60
$CCAA_2$	773	2.0	100	0.65
$AC_{commercial\ (1)}$	-	-	90	0.57
$AC_{commercial\ (2)}$	-	-	100	0.61

Table 4.1 Shows the physical properties of activated carbon from corn cob with activation using zinc chloride. The pore volume was obtained from the adsorption of Nitrogen at 78 K.

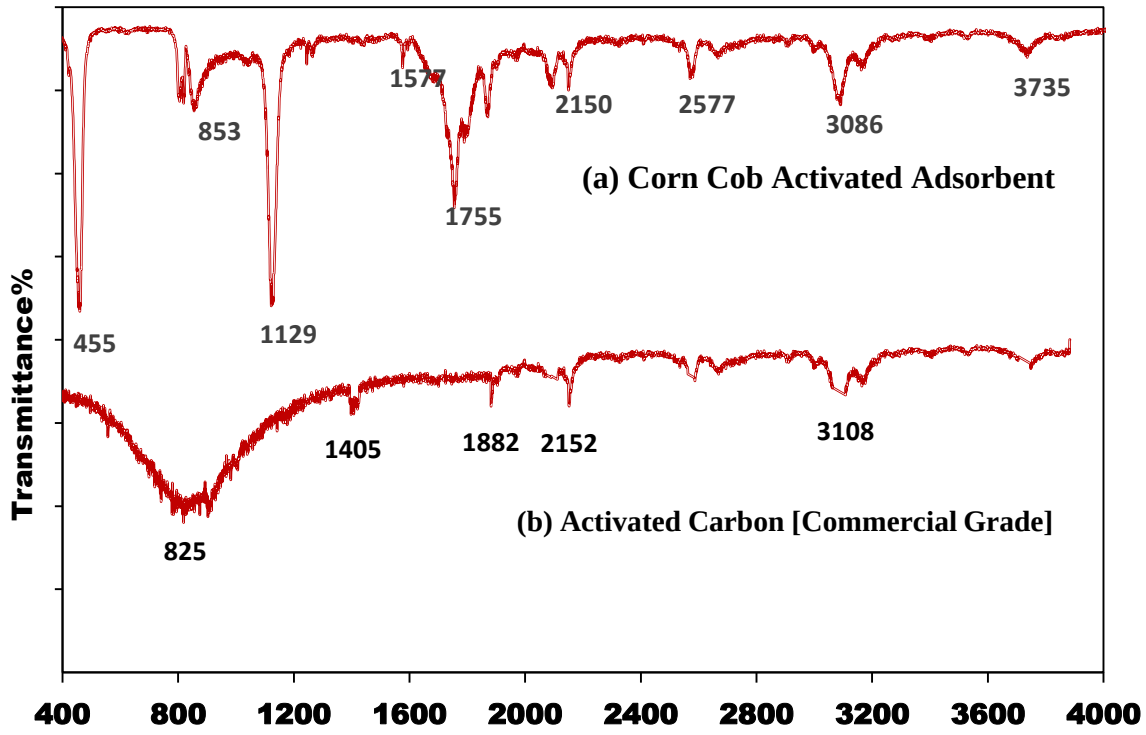

Fig 4.3: FT-IR Spectra for (a) Corn Cob Activated Adsorbent & (b) Activated Carbon (Commercial Grade)

Fig 4.3 shows the FTIR bands attained from the spectrum of solid phase CCAA (a) and that of (b) $AC_{commercial}$. The CCAA peak intensities shown are almost similar although those of CCAA are sharper than the broader bands in $AC_{commercial}$, which is supposed to be compensated by improved chemical characteristics of CCAA by chemical activation plus impregnation unlike in $AC_{commercial}$. In Fig 4.3(a) AACC spectrum, the bands visible in region from 1755 cm^{-1} to 455 cm^{-1}, showing highest peaks at 1755 cm^{-1}, 1129 cm^{-1}, 853 cm^{-1}, 809 cm^{-1} and 455 cm^{-1} confirms stretches within the CCAA which are characteristics of aliphatic functional groups - CH_3 and -CH_2-. (Ketcha, et al., 2012) reported same findings on activated carbons from maize cobs by $ZnCl_2$. The 3086 cm^{-1} and 3735 cm^{-1} peaks vibrations propose the occurrence of hydroxyl (OH) groups and chemically sucked up water on the surface. (Alves, 2013). Band evident at around 3086 cm^{-1} confirms the functional –OCH_3 and that around 3735 cm^{-1} confirms C=O stretching. The confirmations are described in connection to the availability of lignin and hemicellulose esters (Alves, 2013). Note that the bands are less apparent in $AC_{commercial}$ equated to the bands found in CCAA. It is highly probable that the result is in relation to the hydrolysis of lignin and hemicellulose. The decrease in bands intensities following activation might be related to interfaces of the hydroxyl with the activating agent. Conclusively the marginal transformation separating the CCAA bands to those of $AC_{commercial}$ approves the activation of the CCAA.

4.2.2 Point zero charge determination

Table 4.2 Point zero charge data (pHpzc)

Sample ID	pH	pHpzc
CCAA$_1$	7.4	1.9
CCAA$_2$	7.9	2.0
AC$_{commercial\ (1)}$	7.5	1.9
AC$_{commercial\ (2)}$	8.1	2.3

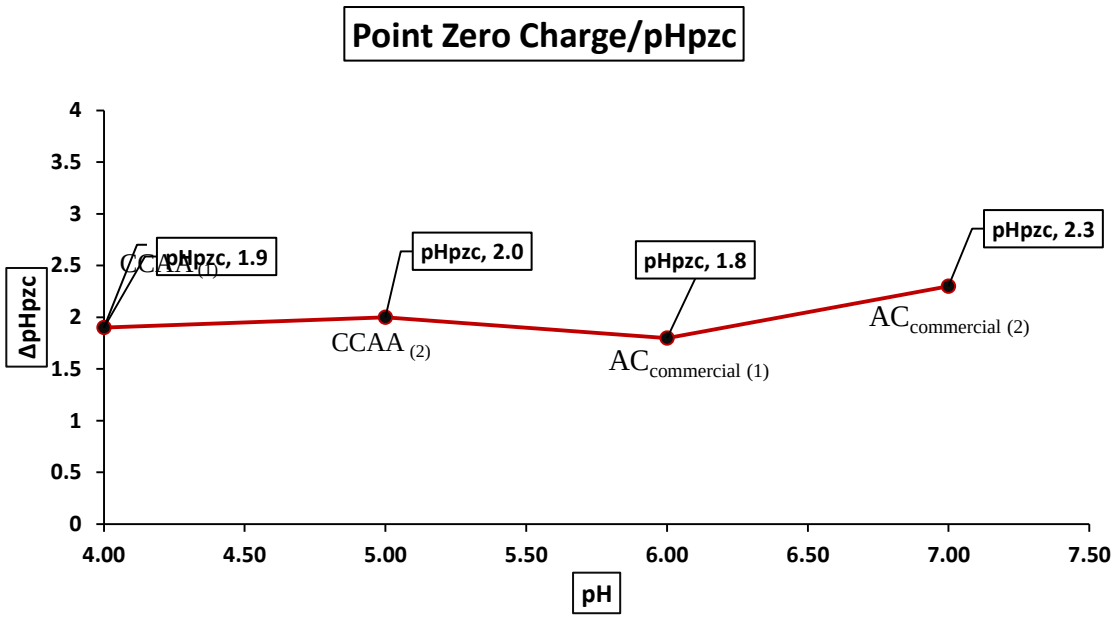

Fig 4.4: Point Zero Charge

The charge on the adsorbent surface, CCAA and $AC_{commercial}$, is characterized by the pHpzc shown in fig 4.5. The higher the pHpzc value, the more positive the surface is and the reverse is true for lower pHpzc value. pHpzc for the synthesised CCAA were 1.9 and 2.0 and $AC_{commercial}$ were 1.8 and 2.3. CCAA having an average pHpzc of 1.95 being less positive to that of $AC_{commercial}$ with pHpzc equal to 2.05.

4.2.3 Effect of contact time

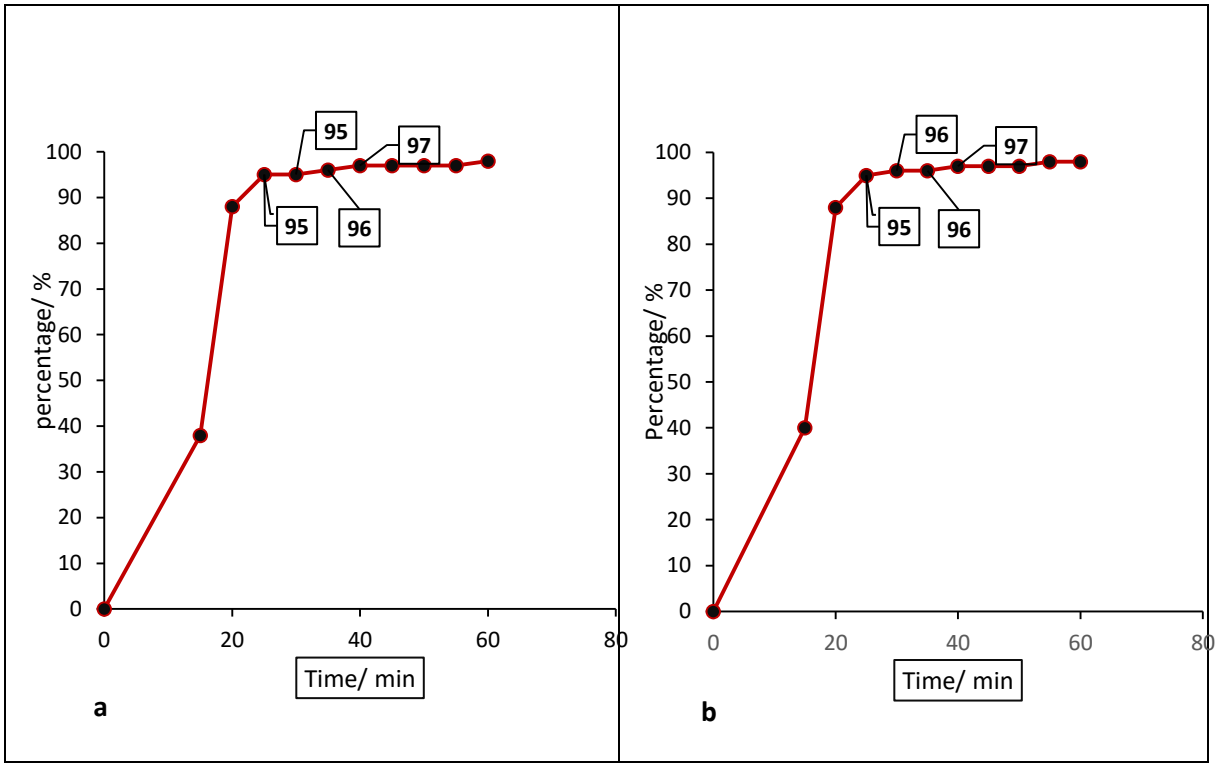

Fig 4.5: Effect of Contact time on % removal of CN^- (a) $AC_{commercial}$ (b)CCAA

Adsorption rate is directly proportional to increase in contact time since there is sufficient increase in the number of adsorption points for CCAA (Alves, 2013). (Rajesh Roshan Dash, 2009) reported a rapid increase in cyanide concentration removal in the initiation of the adsorption mechanism followed by retardation at a later time interval. (Rajesh Roshan Dash, 2009) further stated that the slow step is considered to be a result of diffusion of CN^- from the bulk wastewater solution to the active surface sites. Fig 4.4(a) and (b) shows the seemingly sharp increase from the initiation of the process to 15 minutes in both CCAA and $AC_{commercial}$ graphs succeeded by that from 15 minutes to 20 minutes which is evident of the randomised adsorption at the unoccupied adsorption sites. The slight increase from 20 minutes to 30 minutes is resultant of active site limitation. Lastly, the low to no change in the parts 30 minutes to 60 minutes confirmation that all active positions on the CCAA and $AC_{commercial}$ are fully occupied.

4.2.4 Effect of adsorbent dosage

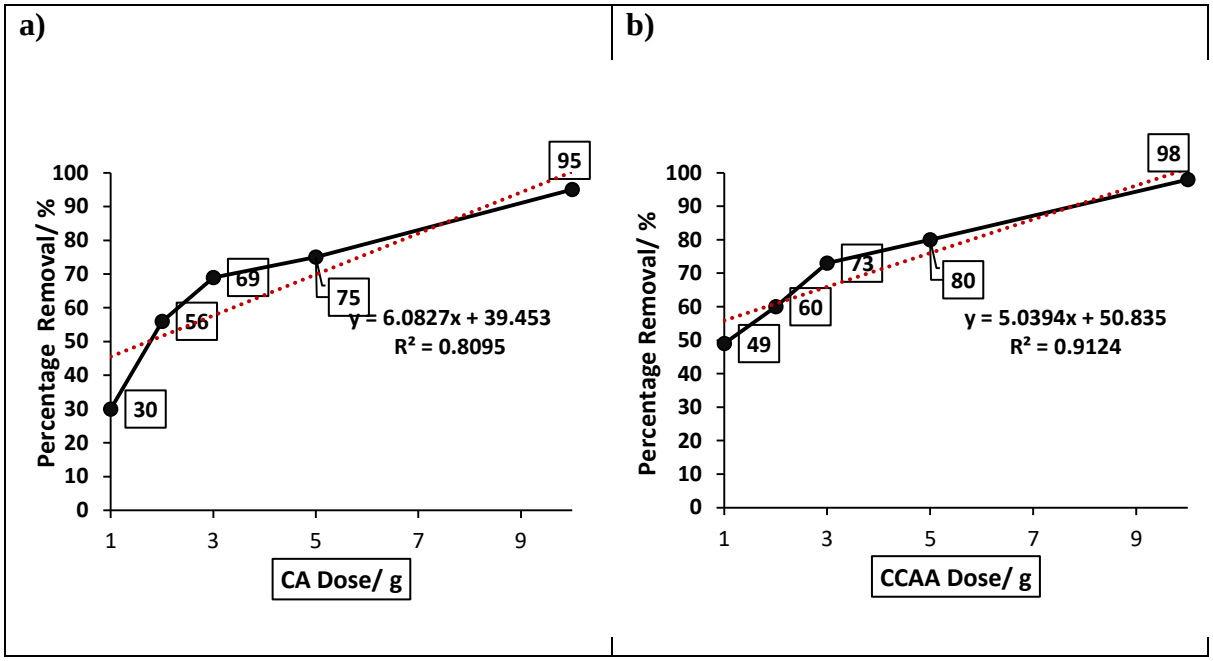

Fig 4.6: Dosage effect adsorbent dosage on % removal (a) $AC_{commercial}$ Dosage (b)CCAA Dosage

Fig 4.7(a) and (b) shows the dosage impact of adsorbent. The dosage impact increases directly proportional to the percentage removal of the free cyanide (Foereid, 2015). (Foereid, 2015) further reported the reason being that the number of active sites ready to absorb the cyanide compound is increased with the increases in the CCAA hence the increase in the overall removal increases. The same applies to the $AC_{commercial.}$ The validity of proportions of the percentage removal of CN^- to CCAA and $AC_{commercial}$ dosage is illustrated in figure 4.7(a) and (b) by the regression $R^2 = 0.9124$ for CCAA and $R^2=0.8095$ for $AC_{commercial}$.

4.2.5 Temperature Effect

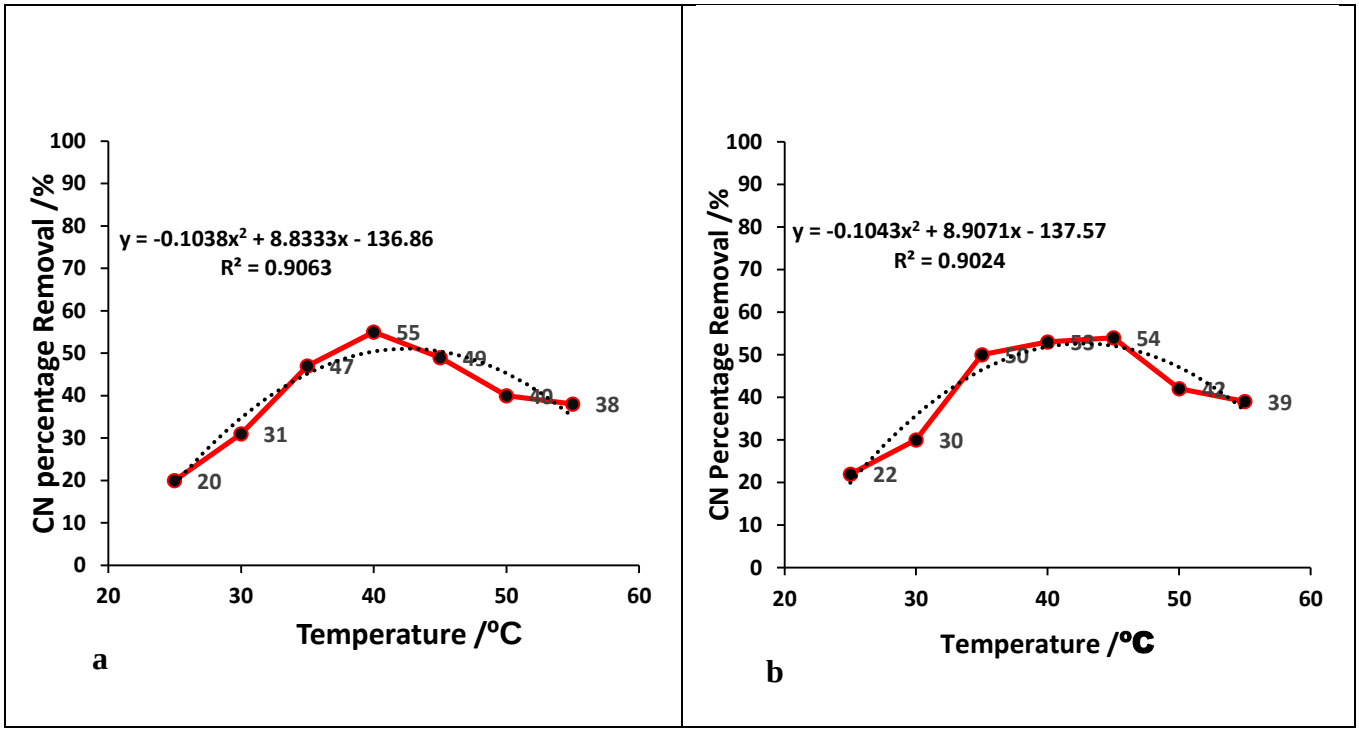

Fig 4.7: Effect of temperature effect on % removal (a)CCAA (b) $AC_{commercial}$

Temperature increase at instant is directly proportional with an increase in the rate of degradation process of the free cyanide until a maximum temperature is reached and the rate is reduced (Manal A. El-Sheeta, 2022) . *Fig 4.5(a)* and *(b)* shows the outcome attained as a result of reduced adsorption of the free cyanide on the surface of CCAA and $AC_{commercial}$ evident by a maxima at a low temperature of 40 ^{o}C for CCAA and 45 ^{o}C for $AC_{commercial}$. For the CCAA, from 25 ^{o}C to 40 ^{o}C the temperature increases has a significant increase in adsorption percentage of the reactants and there are chances of desorption after 40 ^{o}C evident by the decrease in the cyanide removal percentage as at that temperature and onwards (Rajesh Roshan Dash, 2009). The initial increase in temperature favours adsorption of the reactant which is a spontaneous endothermic occurrence. Additionally, the increasing in temperature correspondingly has preferences in the desorption of the final reaction product, whose desorption tends to impede the forward reaction. (Rajesh Roshan Dash, 2009) reported

adsorption process to be exothermic in nature and tents to decrease the rate of adsorption with increase in temperature.

4.2.6 Effect of pH

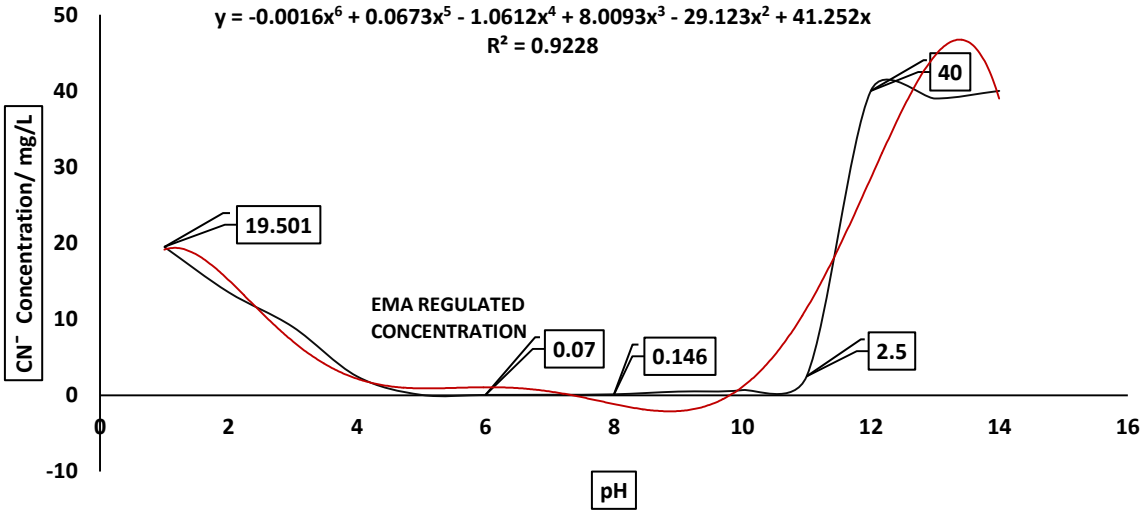

Fig 4.8: Optimised pH Curve

Fig 4.9 shows the pH effect as well as the optimum pH level suitable free cyanide detoxification occurring at pH = 6, where the expected and regulated concentration of 0.07 mg/L is achieved in the detoxification experiment. The result means that the pH must always be corrected and regulated to a pH of 6 for effective detoxification. (Rajesh Roshan Dash, 2009) reported a significant optimum adsorption and reduction in cyanide concentration at pH 6 to 7. Rajesh stated that at pH high or lower than the range, adsorption is minimised due to dissociation of the cyanide compound.

4.2.7 UV-Vis calibration curve

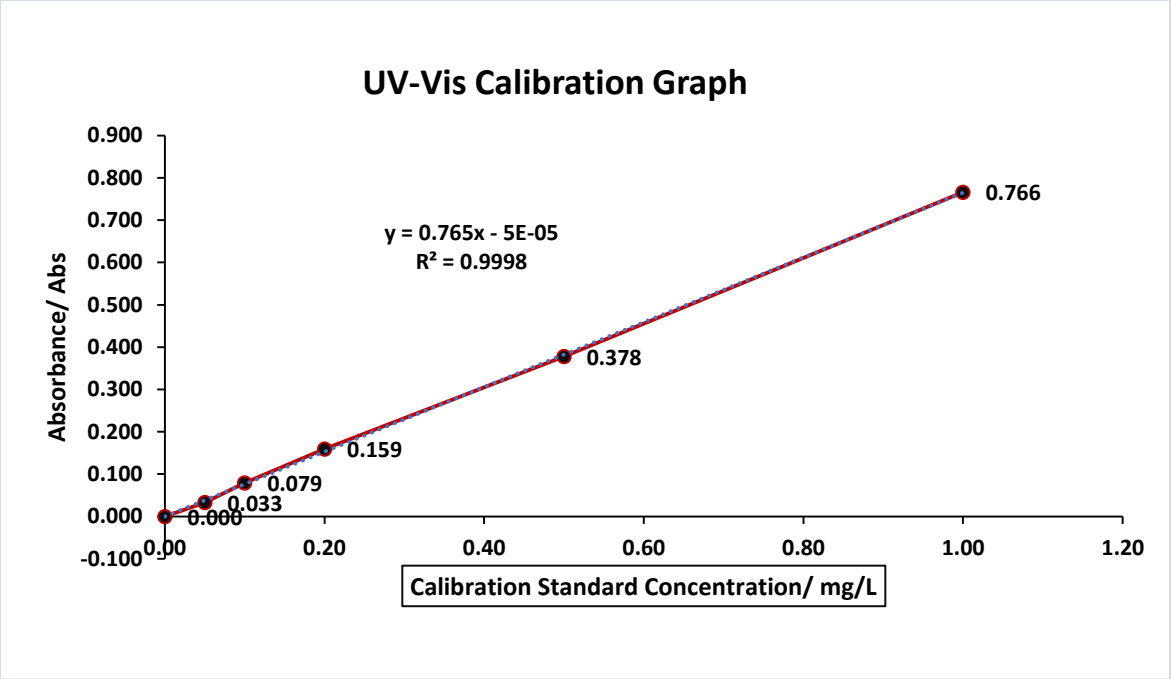

Fig 4.9: UV-Vis Calibration Graph

Fig 4.8 shows the calibration graph of free cyanide analysis method using pyridine-barbituric chemical used to determine the cyanide concentration on the UV-Vis (PGI T60, China**)** spectrophotometer (Rodger Baird, 2017). Shown is a linear progression with equation **y =** 0.765x-5E-05 which has R^2 = 0.9998. Centred on the justification by the results, the method can be used to define the free cyanide concentration by use of the pyridine-barbituric reagent with a UV-Vis (PGI T60, China) spectrophotometry finish (Rodger Baird, 2017).

4.2.8 Adsorption Isotherms

Langmuir

Table 4.3: Langmuir adsorption data

Volume (L)	Mass (g)	Ci (mg/L)	Qe	Ce (mg/L)	Ce/Qe
0.1	2	20	0.409	11.83	28.96
0.1	2	40	0.755	24.89	32.96
0.1	2	60	0.961	40.79	42.47
0.1	2	80	1.229	55.42	45.09
0.1	2	100	1.461	70.79	48.47

Freundlich

Table 4.4: Freundlich adsorption data

Freundlich

Volume (L)	Mass g	Ci mg/L	Ce (mg/L)	1/Ce	qe	1/qe	logCe	log(qe)
0.1	2	20	5.915	0.169	0.704	1.420	0.772	-0.152
0.1	2	40	13.634	0.073	1.318	0.759	1.102	-0.120
0.1	2	60	20.811	0.048	1.959	0.510	1.318	0.292
0.1	2	80	27.082	0.037	2.646	0.378	1.433	0.423
0.1	2	100	34.065	0.029	3.297	0.303	1.532	0.518

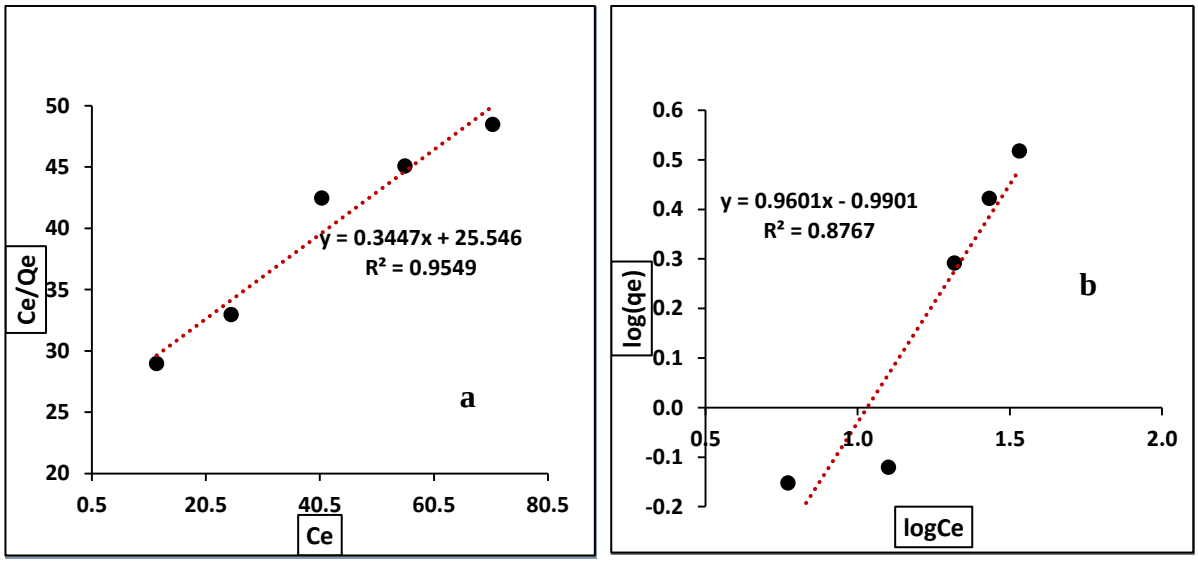

Fig 4.10: Adsorption Isotherms (a)Langmuir (b) Freundlich

4.2.9 Adsorption Kinetics

Table 4.5: Adsorption kinetics data

Kinetics

Time minutes	Ci mg/L	Ce mg/L	qt mg/g	Qe	(qe-qt)	t/qt	ln(qe-qt)
15	100	69.53	30.47	98.539	68.069	0.492	4.221
30	100	62.32	37.68	98.539	60.859	0.796	4.109
45	100	42.43	57.57	98.539	40.969	0.782	3.713
60	100	39.47	60.53	98.539	38.009	0.991	3.638

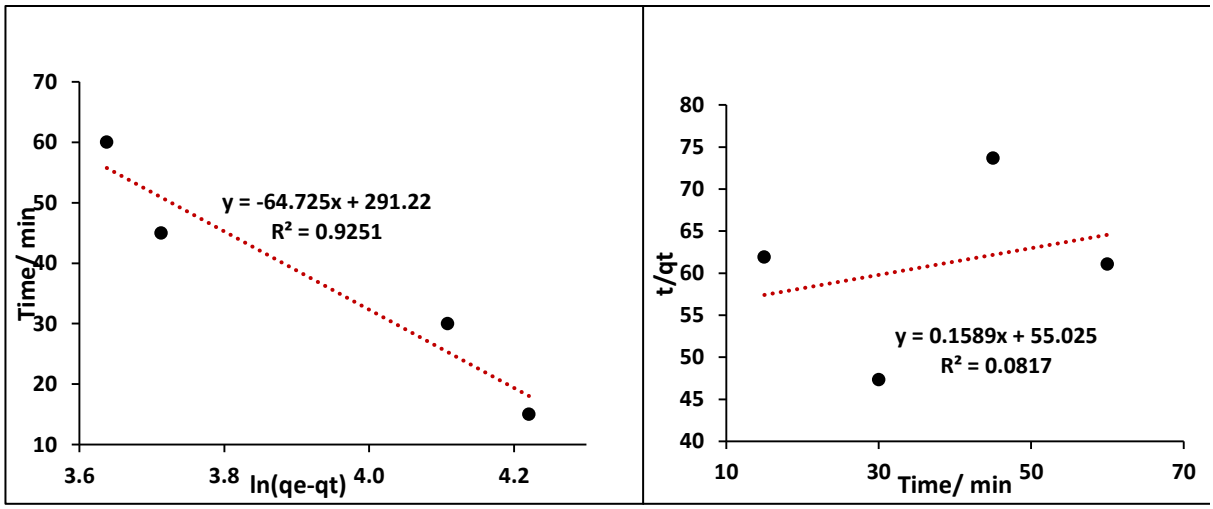

Fig 4.11: Adsorption Kinetics (a)1st Order Pseudo (b)2nd Order Pseudo

Table 4.6: Adsorption Isotherm and Reaction Kinetics data

	Adsorption Isotherm and Reaction Kinetics Parameters			
	Isotherm Models		Reaction Kinetics	
	Langmuir	Freundlich	Pseudo first-order	Pseudo second-order
Linear Equation	**y = 0.3447x + 25.546**	**y = 0.9601x - 0.9901**	**y = -64.725x + 291.22**	**y = 0.1589x + 55.025**
Coefficients	**Kl = 0.01349**	**Kf = 2.69**	**K1 = 149.061**	**K2 = 0.000464**
	Qm = 2.90 mg/g	**1/n = 0.96**	**Qe = 2.9E126 mg/g**	**Qe2 = 39.160 mg/g**
R^2	**R^2 = 0.9549**	**R^2 = 0.8767**	**R^2 = 0.9251**	**R^2 = 0.0817**

The data achieved from the experiment imply that adsorption of free cyanide on CCAA obeyed the Langmuir model in Fig 4.7 (Gedam, 2019)compared to the Freundlich model in Fig 4.8, to a greater extend due to the marginal difference in R^2 values which were computed to 0.9549 for Langmuir and 0.8767 for Freundlich as indicated in the tabulated data in Table 4.6. The Langmuir model confirms the development of monolayer and even distribution of the CCAA (Xiao, 2018). The Langmuir model also confirms the high adsorption capacity of the CCAA to be 2.90 mg/g noted by Q_m.

For the kinetic models, the CCAA has shown to be compatible with the pseudo first-order models (Gedam, 2019) in fig 4.9 with a greater R^2 value of 0.9251, compared to that of the pseudo second-order moder in fig 4.10 with R^2 equal to 0.0817. The K_1 (149.061) in the pseudo first order was far greater that the K_2 (0.000464) in the pseudo second-order (Gedam, 2019). The CCAA is also confirmed to follow pseudo first-order due to the marginally high equilibrium adsorption capacity of $2.9x10^{12}$ mg/g compare to that of the pseudo second-order at 39.160 mg/g denoted by Qe and Q^2_e respectively.

4.2.10 Thermodynamics

Table 4.7: Thermodynamics Raw Data

Temp	Kelvin	1/T	lnKL	KL	Ce	Qe	ΔG
25	298	0.00336	0.3487	1.4172	69.530	98.539	-11.5379
35	308	0.00325	0.4582	1.5812	62.320	98.539	-20.1461
45	318	0.00314	0.842597	2.3224	42.430	98.539	-28.7542

Intercept	Slope	R^2	R $Jmol^{-1}k^{-1}$	ΔH $KJmol^{-1}$	ΔS $Jk^{-1}mol^{-1}$
7.1568	-2036.8	0.9261	8.314	244.98	0.8608

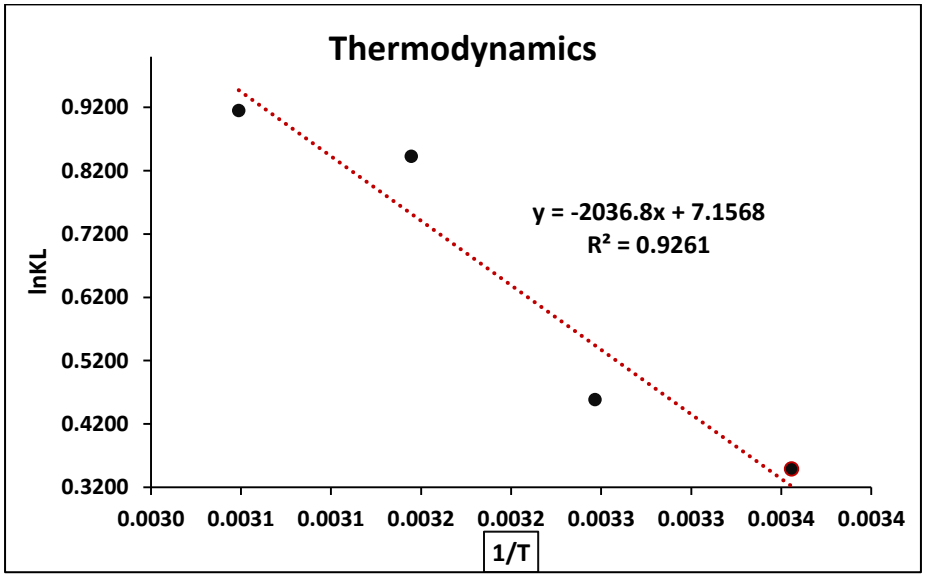

Fig 4.12: van't Hoff plot

The thermodynamic considerations for the detoxification of free cyanide by CCAA is featured by van't Hoff plot (Gedam, 2019) shown in the figure 4.14 computed from the data presented in table 4.7. Gibbs free energy values calculated from the data obtained using the equation 3.11 at different temperatures and the negative ΔG values indicate that the reaction was spontaneous and achievable (Makrigiann, 2015). The most spontaneous reaction denoted by ΔG, was observed at 318 K which was -28.7542 followed by at 308 K at -20.1461 which was successive to that at 298 K with ΔG equal to -11.5379. The decrease in negativity of the ΔG is effected by a decrease in temperature, therefore the reaction becomes less favourable with the decrease in

temperature although for the indicated temperature (298 K, 308 K, 318 K), the reaction was spontaneous. The positive enthalpy change (ΔH), of reaction shows that the experiment for the cyanide detoxification by CCAA is endothermic. The entropy (ΔS) for the detoxification experiment was 0.8608 J k^{-1} mol^{-1} also is evidence that the reaction is spontaneous (Muhammad Khairud Dahri, 2015).

Other relating research findings on carbon Adsorption Capacities has been mentioned in Table 2.2

Chapter 5 : CONCLUSION AND RECOMMENDATIONS

5.0 INTRODUCTION:

The chapter summarize the overall findings and a conclusion is drawn from the experimental exercise as well as recommendations that can aid enhancement of method used and to explore the uncovered scope in the current work.

5.1 CONCLUSION

The experimental study was successful, optimum condition for free cyanide removal from wastewater using corn cob activated adsorbent (CCAA) were established. At pH 6 the final concentration of free cyanide in the isolated sample bin was reduced from an initial concentration of 179 mg/L to 0.07 mg/L, significantly equal to the permitted discharge limit according to EMA regulations. Other findings supporting the results:

1. Adsorption method obeyed the Langmuir model.
2. Adsorption performances followed the pseudo-first order model.
3. Thermodynamic studies showed that the reaction was spontaneous and endothermic

Although seemingly results have been established in the reports from Chapter 4 between the commercially available Activated adsorbent and the prepared agricultural low-cost adsorbent, conclusively, the Corn Cob Activated Adsorbent effectively reduced the initial free cyanide concentration to allowable limits to a greater extend by detoxifying the noxious compound in wastewater. This makes it an endorsed and prominent adsorbent which can be used in place of the commercially available Activated Carbon thus the main objective of the current study satisfied.

5.2 RECOMMENDATIONS

Complementing researches should focus on methods that can be implemented in regenerating the adsorbent, as well cover improvements on the efficiencies of the adsorbent and lastly methods that can be used in detoxifying other trace elements and ions that are common in geochemical laboratory wastewaters with the aim to improve removal of pollutants in an environmentally acceptable way which is also cost effective and convenient.

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APPENDIX

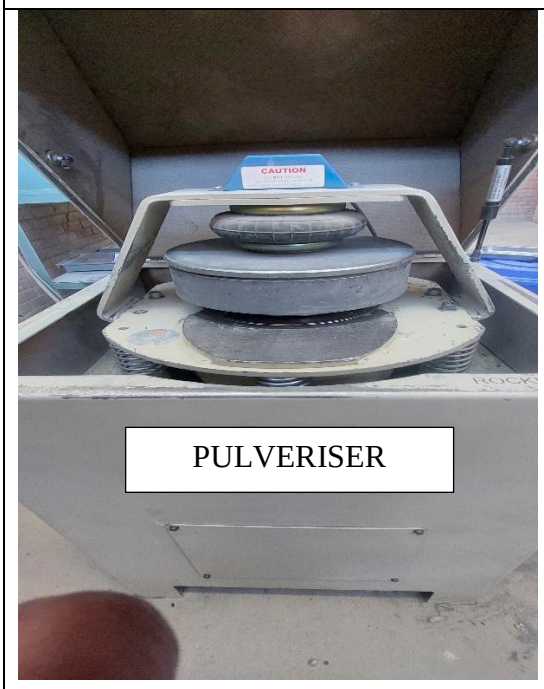

Figure 1: Equipment Used for CCAA Preparation.