REMOVAL OF HEAVY METAL IONS FROM LOCAL BATTERY RECYCLING WASTEWATER USING FUNCTIONALIZED CORN HUSK DERIVED ACTIVATED CARBON

BY

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ABSTRACT

The synthesis of functionalized corn husk derived activated carbon was aimed at studying the potentials of the adsorbent in the removal of heavy metals from local battery recycling wastewater. The synthesis emphasizes on the pretreatment, particle size, amine functionalization and thermal treatment of the adsorbent while the effect of contact time, adsorbent dosage, effluent temperature, pH and concentration forms the basis of the batch adsorption study. The characterization of the raw corn husk and functionalized corn husk derived activated carbon was carried out using thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), Branauer-Emmett-Teller analysis (BET), and scanning electron microscopy-elemental disperse spectroscopy (SEM-EDS). The results of TGA shows a temperature profile with steep degradation between 300 and 500 °C while the FT-IR results reveals the presence of various functional groups before and after modification, the SEM-EDS results also revealed enhanced pores in the activated carbon with broad elemental dispersion containing carbon, nitrogen, oxygen and hydrogen suggests the presence of related functional groups. Effect of contact time was studied between 5 and 140 min while the effect of temperature and dosage were studies between 28 to 70 °C and 0.5 to 5 g respectively. Further study on the effect of concentration and pH were conducted between the ranges of 10 to 100 % effluent initial concentration and 2 to 11 pH respectively. The experimental adsorption capacity (q_e) was 7.95, 6.08 and 4.99 mg/g for Pb Cu and Ni respectively. The Langmuir, Fruendlich, Harkin-Jura, Elovich, Dubinin, Temkin, Jovanovic and D-R isotherms were used to describe the process with a best fit in Fruendlich isotherm which suggests multi-layer adsorption. The study of Pseudo-first, Pseudo second order, Elovich and Intra-particle diffusion kinetic models reveals best fit for second order rate which suggests chemisorption. Further thermodynamic studies also suggest exothermic reaction with negative enthalpy and Gibbs free energy. Desorption study also reveals the viability of the adsorbent for recycle and reuse as 99 % removal efficiency was observed after three cycles.

TABLE OF CONTENTS

Content

Page

9

Cover	page	i
Tittle	page	ii
Decla	ration	iii
Certifi	ication	iv
Ackno	owledgments	v
Abstra	act	vi
Table	of Contents	vii
List of	f Tables	xiv
List of	List of Figures	
List of	f Plates	xvi
CHAI	PTER ONE	
1.0	INTRODUCTION	1
1.1	Background of the Study	1
1.2	Aim and Objectives of the study	4
1.3	Statement of the Research Problem	5
1.4	Justification of the Study	6
1.5	5 Scope of Study	
CHAI	PTER TWO	
2.0	LITERATURE REVIEW	8
2.1	Industrial Effluent Pollution	8

2.2 Physico-Chemical Characteristics of Industrial Effluents

2.2.1	Biochemical oxygen demand	9
2.2.2	Chemical oxygen demand	9
2.2.3	Dissolved oxygen (DO)	9
2.2.4	Oxygen demand	10
2.2.5	Total dissolved solids	10
2.2.6	Total suspended solids	11
2.2.7	Turbidity	11
2.2.8	The pH	12
2.3	Heavy Metals	12
2.3.1	Copper (Cu)	12
2.3.2	Lead (Pb)	13
2.3.3	Iron (Fe)	14
2.3.4	Zinc (Zn)	14
2.3.5	Chromium (Cr)	15
2.3.6	Cobalt (Co)	15
2.3.7	Arsenic (As)	16
2.4	Conventional Methods of Heavy Metal Removal from Wastewater	16
2.4.1	Precipitation	16
2.4.2	Ion exchange	16
2.4.3	Electro-winning	17
2.4.4	Electro-coagulation	17
2.4.5	Cementation	17
2.4.6	Reverse Osmosis and electro-dialysis	18

2.5	Adsorption Process and Mechanism	18
2.6	Adsorption Models	19
2.6.1	Adsorption isotherm	19
2.6.1.1	Langmuir isotherm	20
2.6.1.2	2 Freundlich isotherm	20
2.6.1.3	B Hill-Deboer isotherm	21
2.6.1.4	Fowler-Goggenheim isotherm	22
2.6.1.5	5 Dubinin-radushkevich isotherm	22
2.6.1.6	5 Temkin isotherm	23
2.6.1.7	Flory-huggins isotherm	24
2.6.1.9	Harkin-Jura isotherm	24
2.6.1.9	Jovanovic isotherm	25
2.6.1.1	0 Elovich isotherm	25
2.7	Adsorption Thermodynamic	26
2.7.1	Factors Affecting the Adsorption of Heavy Metals	26
2.7.1.1	Effect of pH	27
2.7.1.2	2 Effect of Temperature	28
2.7.1.3	B Effect of Contact Time	29
2.7.1.4	Effect of Initial Concentration	30
2.7.1.5	5 Effect of Adsorbent Dose	31
2.7.1.6	5 Effect of effluent Flow rate	31
2.8	Desorption and Regeneration of Heavy Metals from Sorbent	31
2.8.1	Desorbents Used for Heavy Metals	34

2.8.1.1	Hydrochloric acid	34
2.8.1.2	Nitric acid	35
2.8.1.3	Sulfuric acid	35
2.9	Low Cost Adsorbents	36
2.10	Volume and Pore Size Distribution	39
2.11	Analytical Tools	41
2.11.1	Fourier Transform Infrared Spectroscopy (FT-IR)	41
2.11.2	Scanning Electron Microscope (SEM)	42
2.11.3	Atomic Absorption Spectroscopy (AAS)	43
2.11.4	Branauer-Emmett-Teller (BET)	44
2.12	Proximate and Ultimate Analysis	46
СНАР	TER THREE	
3.0	MATERIALS AND METHODOLOGY	47
3.1	Overview of Material and Methodology	47
3.2		
	Materials	47
3.3	Materials List of Equipment Required	47 48
3.3 3.4	Materials List of Equipment Required Preparation of Raw Materials	47 48 49
3.33.43.4.1	Materials List of Equipment Required Preparation of Raw Materials Adsorbent preparation	47 48 49 49
3.33.43.4.13.4.2	Materials List of Equipment Required Preparation of Raw Materials Adsorbent preparation Proximate analysis	4748494950
 3.3 3.4 3.4.1 3.4.2 3.4.2.1 	Materials List of Equipment Required Preparation of Raw Materials Adsorbent preparation Proximate analysis Moisture content	 47 48 49 49 50 50
 3.3 3.4 3.4.1 3.4.2 3.4.2.1 3.4.2.2 	Materials List of Equipment Required Preparation of Raw Materials Adsorbent preparation Proximate analysis Moisture content Ash content	 47 48 49 49 50 50 51
 3.3 3.4 3.4.1 3.4.2 3.4.2.1 3.4.2.2 3.4.2.3 	Materials List of Equipment Required Preparation of Raw Materials Adsorbent preparation Proximate analysis Moisture content Ash content Volatile organic carbon	 47 48 49 49 50 50 51 51

3.4.2.5	Acid pretreatment	51
3.4.3	Adsorbent modification	52
3.4.3.1	Amination reaction	52
3.4.3.2	Corn husk based activation carbon	54
3.4.4	Adsorbent characterization	54
3.4.5	Effluent collection and analysis	54
3.4.6	Adsorption test	55
3.4.6.1	Batch adsorption study	55
3.4.6.2	2 Desorption study	57
СНАР	TER FOUR	
4.0	RESULTS AND DISCUSSION	58
4.1	Collection of Result and Interpretations	58
4.1.1	Proximate analysis	58
4.1.2	Thermo Gravimetric analysis	58
4.1.3	Thermal activation	59
4.1.4	Effluent analysis	60
4.2	Adsorbent Characterization	60
4.2.1	Functional group composition	60
4.2.2	Surface morphology	63
4.2.3	Surface area and pore volume	65
4.3	Adsorption Studies	66
4.3.1	Effect of contact time	66

4.3.2	Effect of adsorbent dosage	
4.3.3	Effect of temperature	
4.3.4	4 Effect of concentration	
4.3.5	Effect of solution pH	71
4.4	Adsorption Isotherm Models	73
4.5	Adsorption Kinetic Models	78
4.6	5 Thermodynamic Study	
4.7	Regeneration Study	
CHAI	PTER FIVE	
5.0	CONCLUSIONS AND RECOMMENDATIONS	82
5.1	Conclusions	82
5.2	Recommendations	83
5.3	Contribution to Knowledge	
REFE	REFERENCES 8	
APPE	APPENDICES	

LIST OF TABLES

Table	Title	Page
2.1 Previous works on functionalize	d adsorbents	38
2.2 IUPAC classification of pore siz	ze (2017)	41
3.1 List of materials and reagents us	ed	48
3.2 Lists of equipment used		49
3.3 Experimental variables		56
4.1 Proximate analysis result		58
4.2: Thermal activation of F-CHAC		60
4.3 preliminary effluent analysis		60
4.4 Comparison of FTIR peaks and	band positions	63
4.5 Comparison of BET analysis res	sult with literature	67

4.6 Adsorption isotherm parameters for Pb, Cu and Ni	76
4.7 Comparison of F-CHAC's adsorption capacity with literature works	78
4.8 Adsorption kinetic parameters of Pb, Cu and Ni	79
4.9 Thermodynamic parameters for Pb, Cu and Ni removal	81
4.9 Desorption and recovery efficiency of F-CHAC	82

LIST OF FIGURES

Figures	Title	Page
3.1 Synthesis pathway for CHP fun	ctionalization through amination reaction	53
4.1 TGA Analysis of Raw corn hus	k	59
4.2a FT-IR Result of raw corn husk		64
4.2a FT-IR Result of F-CHAC		64
4.3a Morphology of raw corn husk,	,	65
4.3b Morphology of F-CHAC,		65
4.3c EDS of raw corn husk		66
4.3d EDS of F-CHAC		66
4.4 Effect of contact time on the ad	sorptive removal of Pb, Cu, and Ni	68
4.5 Effect of adsorbent dosage on the	he adsorptive removal of Pb, Cu, and Ni	70
4.6 Effect of temperature on the ads	sorptive removal of Pb, Cu, and Ni	71
4.7 Effect of concentration on the a	dsorptive removal of Pb, Cu, and Ni	72

4.8 Effect of solution pH on the adsorptive removal of Pb, Cu, and Ni	74
4.10 Removal efficiency of F-CHAC after 5 cycles	82

LIST OF PLATES

PLATE	Title	Page
I Corn husk waste		47
II A: Dried, B: Crushed	and C: Segregated corn husk	50
III Raw corn husk acid p	retreatment	52

IV Functionalized corn husk based activated carbon

54CHAPTER ONE

1.0 **INTRODUCTION**

1.1 **Background of the Study**

With rapid industrial development, problems related to pollution are becoming severe and water pollution is one of the most serious problems because inorganic and organic wastes are discharged to the aquatic environment either in water soluble or insoluble forms (Abdi and Kazemi, 2015). It has been discovered that nature can cope with small amount of pollutants but it will have high negative impact or almost becomes uncontrollable if the unquantifiable amount of wastewater and sewages released into the environment continuously are not remedied before discharge. Thus, effluent treatment reduces pollutants in wastewater to an acceptable limit which will have no significant impact on human health (Zhou *et al.*, 2013).

Recently, heavy metal ions have become significant pollutants which have detrimental effects on the ecosystem due to the increasing number of production and processing companies (fuel producing, energy, fertilizer, mining, leather, pesticide, metal surface treating, and aerospace etc.) (Chaturvedi and Sahu, 2014). Wastewater treatment systems are designed to reduce metal contaminants to meet discharge requirements and achieve the water quality level needed for reuse and recycling (Adetokun et al., 2018). As a result of improper treatment prior to discharge, many dissolved metals have been found in harmful concentrations in ground waters which are destined for potable drinking water. In small quantities, certain heavy metals are nutritionally essentially for a healthy life, many of these metals are required by human in trace amounts, but in larger, persistent dosages, these heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues and may cause acute or chronic toxicity. The metals which are linked to human poisoning include copper, nickel, cadmium, chromium, arsenic, lead and mercury. Heavy metal toxicity can result in damaged or reduced mental and central nervous function which usually cause learning disabilities, lower energy levels, and damage of blood composition, lungs, kidneys, liver, pancreas and other vital organs which often result in death (Arquilada et al., 2018).

Several treatment methods have been considered in treating wastewater which includes precipitation, ion exchange, electrochemical treatment, and adsorption (Lin *et al.*, 2019), most of the methods suffer some setback like generation of secondary pollutants, expensiveness or low efficiency for minute heavy metal concentration (Ofudje *et al.*, 2015).

12

Adsorption is a greatly preferred method for the treatment of heavy metal ions in wastewater treatment, generally due to its high efficiency, simplicity in handling, high availability of raw materials as well as its cost effectiveness (Nemes and Laura, 2018). Besides, adsorption technology also has the ability to remove and then recover and recycle some of the useful waste materials (e.g. metals) from the wastewater which can help to reduce cost and as such, the demand for adsorbents are increasing as more industries are required to produce their wastewater under a stricter condition as regulated by law (Shaikh *et al.*, 2018).

Activated carbon is one of the most common types of adsorbent used in wastewater treatment. It is highly porous and therefore possessing large surface area, which ranges from 800 to 1200 m²/g. The large surface area of the activated carbon contributes to the adsorption process itself since there are more reactive sites for the adsorbate to bind on the surface of the activated carbon (Adetokun *et al.*, 2018: Abdi and Kazemi, 2015). However, commercially available activated carbon has some existent problems such as a rather high cost, low regenerability and so on, and these restricted their wide usage in wastewater treatment especially for some developing countries (Dawood *et al.*, 2017).

The synthesis of an alternative adsorbent to replace expensive activated carbons and synthetic resins is a field that has recently seen an intensification of interest (Satayeva et al., 2018). Natural materials like bagasse, zeolite, red mud, clay, organic wastes, industrial waste etc., are used for adsorption because of their low cost and high adsorption efficiency. Agro-wastes are considered for the development of activated carbon by several researches due to two important features: renewability and low cost (Hashemian *et al.*, 2017). Agro-wastes such as cashew nut shell (Yahya *et al.*, 2020a), rice husk (Shamsollahi and Partovinia, 2019), potato peels (Edris *et al.*, 2017), corn cob (Ani, 2020), corn stalk (Wen *et al.*, 2018), corn husk (Ismail 2016) and sugarcane

baggers (Abdelwahab *et al.*, 2021) are some of those used as feedstock for the synthesis of adsorbent. Bjorklund and Li (2017) also reported the synthesis of activated carbon from sewage sludge. Preparation of adsorbent by utilizing waste biomass reduces the adsorbent cost and this process is also helpful in waste management.

The presence of amino, sulphate, hydroxyl, nitro, sulphydryl, carboxyl, phosphate, phenol, amides etc. in the structural content of agricultural wastes which produces a binding surface for heavy metals adsorption (Nemes and Laura, 2018; Zhou *et al.*, 2013) gives it an edge in its synthesis for the purpose of treating heavy metal pollution in industrial effluents.

Corn is one of the staple foods consumed globally at large scale because of its relative abundance as it is a major annual crop cultivated world wild with a global index of over a billion metric tons per annum which produces large volume of waste (Priya and Chandrajit 2014), corn is mostly known to possess great potentials among major food crops for achieving break through that will improve food production in Nigeria (Igwegbe *et al.*, 2021). It also generates a large amount of waste corn husk and a few studies have been conducted that used this waste for adsorbent preparation (Mishra *et al.*, 2019; Lin *et al.*, 2019; Ani *et al.*, 2020; Indah *et al.*, 2018; Ismail 2015).

The trend in the research of corn husk powder (CHP) adsorbent has extensively proven the suitability of the adsorbent for heavy metal remediation, various researcher have used several techniques to enhance the adsorption of different pollutants onto CHP adsorbent which include Co-doped (Oana *et al.*, 2013), EDTA modified (Priya and Chandrajit 2014), Chemically Activated carbon (Anton *et al.*, 2018) using various modification processes. This research work seeks to further enhance the process of adsorption of metal ions onto CHP, a novel bio-adsorbent has been considered for activated carbon using CHP-based wastes materials as precursor. A modification process involving co-functionalization by certain amination reactions that will introduce several special nitrogen-containing functional groups is employed which will improve the adsorbent framework and its specific adsorption capacity and expand the scope of utilization of the adsorbent. The characteristics and performance of the prepared functionalized CHP-based activated carbon (F-CHPAC) are also investigated in the context of the above descriptions.

1.2 Aim and Objectives of the Study

This research is aimed at synthesizing a functionalized CHPAC bio-sorbent for the removal of heavy metals from a local battery recycling wastewater. The specific objectives are;

- Preparation of corn husk adsorbent with detailed proximate analysis and as well conducting detailed elemental analysis on the targeted effluent obtained from point source.
- 2. Modification of raw adsorbent by unclogging the adsorbent pores and enhancing the overall pore structure through chemical pretreatment, amination reaction, and heat treatment (Carbonization)
- 3. Characterization of the modified adsorbent using thermo-gravimetric analysis to determine the thermal stability and the fraction of volatile component of the adsorbent, FTIR, porosity and surface area of the adsorbent through BET analysis, surface morphology and elemental analysis of the adsorbent through SEM-EDS analysis.
- 4. Batch adsorption and the study of the effect of some process variables (concentration, dosage, contact time, pH and temperature) on rate of adsorption

- 5. Study the isotherms, kinetic models and thermodynamics of the sorption process
- 6. Investigation of the reusability of the adsorbent and its recovery efficiency through desorption study.

1.3 Statement of the Research Problem

Industrialization has become a global issue as the release of uncontrollable toxic effluents into the environment is on the rise, these effluents cause serious hazards to mankind especially when released into the atmosphere through some mediums. These include the solid, liquid and the gaseous mediums or careers. Heavy metals have been used in various industries for centuries. For the past three centuries the production of heavy metals such as lead, zinc and copper has increased substantially (Ani *et al.,* 2020), Examples of such pollutants include wastewater from paint processing, mining, battery recycle and electroplating.

Local battery recycle has become a common practice in our society as it offers cheap and economical alternative to wet cell battery replacement, used wet cell batteries are collected from different sources and restructured to suit the immediate needs through replacing of damaged cells, spent electrolytes or electro-induction. This and other processes lead to the release of toxic metals into the environment directly or indirectly through water drains, leaching or runoff.

Numerous efforts have been made by researchers to produce composite, functionalized, magnetized or co-doped adsorbent using various methods. An enhanced adsorbent is usually obtained with better functional groups and pore morphology thus a cheap, eco-friendly and effective modification process is proposed in this study to prepare a composite biosorbent functionalized with amines for enhanced heavy metal removal

using corn husk as the adsorbent precursor. Its reuse as an adsorbent for the remediation of heavy metal ions can help to relieve the effects of disposal of industrial effluents and also increase net gain to such industries. It also help to reduce the amount of pollution generated thereby serving as a utility benefit to corn traders and the general public.

1.4 Justification of the Study

Since the conventional methods of removal are expensive and not easily accessible, based on the fact that various biomasses has different metal binding capacities, biosorption for the remediation of heavy metal ions has provided a means better than physicochemical methods (Satayeva et al., 2018). The biomass which includes waste from fruits, cereals, tuber, and the likes are of high potentials of serving as adsorbent. It has been established that approximately 60% of Nigeria's corn production is processed by the industries for production of malt drink, flour, starch syrup, corn flakes, beer, dextrose and animals feeds. It is on record that Nigeria has an annual maize production above 10 million metric tons. The total land area for maize plantation in Nigeria is approximately 2.5 million hectares with an expectation of about 1.4 metric tons per hectare hence the large amount of waste (cob, tassels, shell and husk) generated become an essential raw material for animal feed production and also utilization as adsorbent The thermal treatment method chosen for the modification of the (FOA 2018). adsorbent is an eco-friendly and economical method which requires little amount of energy.

1.5 Scope of the Study

This study focuses on the preparation of modified adsorbent from agricultural waste (corn husk), the modification procedure is restricted to amine-functionalization. The characterization of the prepared adsorbent is limited to the use of FTIR, SEM-EDS, TGA and BET. Proximate analysis of the adsorbent is limited to the determination of

moisture content, ash content, volatile organic carbon and fixed carbon. Adsorption Study is also restricted to removal of Lead, Copper and Nickel ion and process variables are limited to the study of effect of initial metal ion concentration, adsorbent dosage, effluent temperature, solution pH and contact time.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Industrial Effluent Pollution

The current trend of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment (Cazetta *et al.*, 2018). The rate at which effluents are discharged into the environment especially water bodies has been on the increase as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals. The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment (Adetokun *et al.*, 2018).

Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other break down or degradation process and are permanent additions to the marine environment (Mishra *et al.*, 2018). As a result of this, their concentrations often

exceed the permissible levels normally found in soil, water ways and sediments. Hence, they find their way up the food pyramid. When they accumulate in the environment and in food chains, they can profoundly disrupt biological processes. The primary sources of heavy metal pollution in coastal lagoons are input from rivers, sediments and atmosphere, which can affect aquaculture profitability in certain areas (Shaikh *et al.*, 2018). The anthropogenic sources of heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leather tanning industries, fertilizer industries, pigment manufacturing industries, leachates from landfills and contaminated ground water from hazardous waste sites (Nemes and Bulgariu, 2016: Priya and chandrajit 2014: Chaturvedi and Sahu, 2014: Adetokun *et al.*, 2018: Oana *et al.*, 2013: Yahya *et al.*, 2020c). Heavy metals are also emitted from resource recovery plants in relatively high levels on fly ash particles (Shaikh *et al.*, 2018).

2.2 Physico-chemical Characteristics of Industrial Effluents.

2.2.1 Biochemical oxygen demand

Biochemical oxygen demand (BOD) is the amount of oxygen used by organisms while consuming organic matter in wastewater. It is possible to assess the performance of a wastewater treatment plant by measuring the BOD of the inflow and the outflow. Many factors can influence this test, such as temperature of incubation, dilution rate, nitrification, toxic substances, nature of bacterial seed and presence of anaerobic organisms (Oana *et al.*, 2013).

2.2.2 Chemical oxygen demand

This is the equivalent amount of oxygen needed to break down organic matter under strong oxidizing agents. A strong oxidizing agent is added to quickly break down organic material (Fatehi *et al.*, 2019). The process is much faster to perform than BOD testing since an incubation period is not required. COD, like BOD, is only an approximation of the natural degradation of organic materials in nature. The harsh chemicals may break down more of the organic material than a natural process would. Hence, COD is usually greater than the BOD.

2.2.3 Dissolved oxygen (DO)

Water has the ability to dissolve oxygen molecules and many aquatic creatures depend on dissolved oxygen (DO) for survival. When the level of oxygen gets too low, plants and animals may become impaired or even die. The maximum amount of oxygen water is able to dissolve decreases as water temperature increases. As a result of the temperature effect, aquatic life is more frequently subject to DO stress during the summer. In addition, the breakdown of organic materials in water requires the consumption of DO. Therefore, waters receiving large loads of organic materials may have DO concentrations too low to support healthy aquatic communities (Fatehi *et al.*, 2019).

2.2.4 Oxygen demand

Oxygen demand is the amount of oxygen required to aerobically metabolize a waste. Water usually contains organic material consisting of remnants or wastes of plants, animals, and microbial organisms. If organic material is added to water, it will be decomposed by bacteria through biochemical processes (Adetokun *et al.*, 2018). This is known as the oxidation or the breakdown of organic substances. Oxidation uses DO and thus depletes the DO supply available for aquatic life.

2.2.5 Total dissolved solids

Total Dissolved Solids (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal) suspended form, the operational definition is that the solids must be small enough to survive filtration through a sieve size of two micrometer (Fatehi *et al.*, 2019). The principal application of TDS is in the study of water quality for streams, rivers and lakes. Although TDS is not generally considered as a primary pollutant, it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants. The effluents with high TDS value may cause salinity problem if discharged into irrigation water (Priya and chandrajit 2014).

2.2.6 Total suspended solids

Total suspended solid is the sum of the organic and inorganic solid concentrations that can be subdivided into: suspended solids and organic solids. Suspended solids represent the solids that are in suspension in the water. It is generally comprised of 70% organic and 30% inorganic solids and can be removed by physical or mechanical means. Organic solids which are about 50% of solids present in urban wastewater are derived from the waste products of animal and vegetable life (Fatehi *et al.*, 2019). It is sometimes called the combustible fraction or volatile solids as these can be driven off by high temperature. Inorganic solids are inert substances and are not subject to decay. They include sand, gravel and silt, settled solids and it is a subset of suspended solids and represents that fraction of suspended solids that will settle in a given period. Colloidal suspended solids, refer to solids that are not truly dissolved and yet do not settle readily. They can be referred to as organic and inorganic solids that rapidly decay (Adetokun *et al.*, 2018).

2.2.7 Turbidity

Turbidity is a measure of the water's lack of clarity and is often associated with the possibility of microbiological contamination. Water with high turbidity is cloudy, while water with low turbidity is clear. The more particles in the water, the more light is reflected off the particles and therefore the higher the turbidity or cloudiness. High turbidity decreases the amount of sunlight able to penetrate the water, thereby decreasing the rate of photosynthesis (Fatehi *et al.*, 2019). Reduced clarity also makes the water less aesthetically pleasing, making it less desirable for many water uses. This can lead to problems associated with increased water temperature.

2.2.8 The pH

The pH is the concentration of hydrogen ions in solution and indicates the level of acidity or alkalinity of an aqueous solution. If the pH of wastewater is outside the range 6.5-9.2, there may be considerable interference with biological processes (Adetokun *et al.*, 2018). The pH value of water is determined by the relative concentrations of H⁺ ion and OH⁻ ion. Water with pH of 7 has equal concentrations of H⁺ ion and OH⁻ ion and is considered to be a neutral solution. If a solution is acidic (pH<7), the concentration of H⁺ ion is greater than the concentration of OH⁻ ion. If a solution is basic (pH>7), the concentration of H⁺ ion is less than the concentration of OH⁻ ion. A change from pH7 to pH8 represents a ten-fold increase in the OH ion (Priyantha *et al.*, 2018).

2.3 Heavy Metals

Heavy metals are inorganic components whose density is 5 times denser than the density of water. They are natural components of the earth crust that cannot be degraded or destroyed. These metals enter into living organisms through food or proximity to

emission sources. They tend to bio-accumulate over time, and are stored faster than excreted (Mishra *et al.*, 2019: Cazetta *et al.*, 2018: Gong *et al.*, 2018: Chen *et al.*, 2016: Peng *et al.*, 2017). Some heavy metals found in industrial effluents include: Cu, Pb, Fe, Zn, Cr, Co, As, etc.

2.3.1 Copper (Cu)

Copper is a very common metal that exists naturally in the environment and spreads across the environment through natural phenomena. Two types of copper can be formed: Cu(I) and Cu(II). As industries advance, copper has become one of the most widely used metals. The primary waste sources of copper discharged from industries include printed circuit boards, metal finishing industries, tannery operations, chemical manufacturing and mining drainage (Fu *et al.*, 2016). The production of copper has increased over the last decades, which contributes to the expanded copper quantities in the environment.

Excess amount of copper in the body can inhibit the enzyme dihydrophil hydratase, an enzyme involved in haemopoiesis. An inherited condition called Wilson's disease causes the body to retain Copper, since it is not excreted by the liver into the bile. If this disease is not treated, brain and liver damage can occur. Excessive Copper in water has also been found to damage marine life (Lunge *et al.*, 2014). The observed effect of higher concentrations of copper to fish and other creatures is damage to gills, liver, kidneys and the central nervous system (Fu *et al.*, 2016).

2.3.2 Lead (Pb)

Lead exists in three oxidation states: Pb(O), Pb(II) and Pb(IV). Metallic lead, Pb(O) exists in nature, but its occurrence is rare. In the environment, lead is commonly found combined with two or more other elements to form lead compounds and it usually exists

as Pb(II). Lead occurs naturally in the earth crust but the high level of lead found throughout the environment mainly comes from human activities. The use of leaded gasoline, house paint and pesticides has already been banned in recent years. Lead is still widely used in car batteries and ammunitions. The improper disposal of wastewater from these industries contributes to the environmental rise in lead level. Accumulation of lead in human body causes a rise in blood pressure, abortion, improper function in the brain and kidney as well as behavioral disruption and mental retardation of young children (Mishra *et a*, 2019). Moreover, as lead can enter a fetus through the placenta of the mother, it can also cause damage to the brain and central nervous system of unborn children (Fu *et al.*, 2016).

2.3.3 Iron (Fe)

Iron is an element in the periodic table with an atomic number of twenty six. It is found in the earth crust, often in combination with other chemical elements. Some iron compounds are considered to be soluble in the whole pH range. The availability of iron increases with decreasing pH (Fu *et al.*, 2016). Iron is an essential nutrient, which is involved in the oxygen transport. Proper functioning of the immune system relies in part, on sufficient amounts of iron. The body stores iron very efficiently, and too much of this, can be toxic. Iron overload is a condition characterized by excessive adsorption of Iron through diet. Much of the additional iron is deposited in the liver, damaging the vital organ and causing it to enlarge (Lunge *et al.*, 2014).

Iron overload can lead to a vast range of symptoms like joint pain, constant fatigue, heart problems, hair loss, abnormal liver function, impaired memory, mood swings and depression (Li *et al.*, 2013).

2.3.4 Zinc (Zn)

Zinc is a common element occurring naturally in the environment and it is widely used by humans for domestic and industrial purposes. Zinc compounds are widely used in industries to make paints, rubber, dyes and wood preservatives. Depending on the type of soil, some zinc compounds can percolate into the groundwater, and into lakes, streams and rivers. The solubility of zinc is highly dependent on the compounds, for example zinc phosphate is insoluble and zinc nitrate is soluble (Li *et al.*, 2013). Low level of zinc, Zn(II) is essential for maintaining good health. If zinc levels are too low, it will result in, skin lesions, sexual immaturity, and depression and can affect taste (Igwe and Abia, 2012).

2.3.5 Chromium (Cr)

Chromium is heavy metal on the earth that can also be found in wastewater. It is discharged from the wastewater of the steel manufacturing industry, paint industry, paper industry, electroplating and chrome plated products (Li *et al.*, 2013). Chromium exists in two forms: trivalent Cr(III) and hexavalent Cr(VI). Its abundance is harmful to marine life, vegetation and plants, and to humans due to its toxicity (Lunge *et al.*, 2014). Cr(VI) is also a strong oxidizing agent, as well as a potential carcinogen. Other potential harmful effects on humans due to long term exposure to the metal include liver damage, kidney circulatory damage, and dermatitis (Cazetta *et al.*, 2016).

2.3.6 Cobalt (Co)

Cobalt exists in the principal minerals smaltite (CoAs₂) and Caboltite (CoAsS) and it only represents $4x10^{-3}$ percent of the earth's crust. Cobalt commonly exists in two oxidation states, Co(II) and Co(III). In oxygenated water the Co(II) state is immediately oxidized to the Co(III) state but since the Co(III) state hydrolyzes, its observed concentrations are low (Zhou *et al.*, 2013). Cobalt is used in the preparation of magnetic, wear resistant, and high strength alloys. Its compounds are used in ink, paint, and varnish industries. Cobalt is also a central component of the vitamin, cobalamin, or vitamin B12 and is only slightly toxic. The isotope 60Co is commonly used in radiotherapy, sterilization of medical supplies and medical wastes. But, this high energy gamma emitting isotope can cause severe burns and death (Lunge *et al.*, 2014).

2.3.7 Arsenic (As)

Arsenic is used in paints as preservative. Inorganic arsenic is human poison, organic arsenic is less harmful. In pure form arsenic is a tasteless, odorless white powder or clear crystals. It is not found in pure form in the environment, where it is generally exists combined with oxygen, chlorine or sulfur. These mineral (inorganic) forms of arsenic are generally more toxic than its more complex organic compounds found naturally in animal tissues, especially in fish and sea foods. Arsenic damages many tissues including nerves, stomach intestines and skin. Breathing high levels can cause a sore throat and irritated lungs (Zhou *et al.*, 2013).

2.4 Conventional Methods for Heavy Metal Removal from Wastewater

2.4.1 Precipitation

Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Some metal salts are insoluble in water and get precipitated when correct anion is added. Although the process is cost effective, its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, bisulphate or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration (Lin *et al.*, 2019).

2.4.2 Ion exchange

Ion exchange is a method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solutions as the matrix gets easily fouled by organics and other solids in the wastewater (Xiong *et al.*, 2019). Moreover, ion exchange is nonselective and is highly sensitive to pH of the solution.

2.4.3 Electro-winning

Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like: Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents, this can be recovered by electro-deposition using insoluble anodes (Jassim *et al.*, 2017).

2.4.4 Electro-coagulation

Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants present in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electro-coagulation system, they become destabilized and precipitate in a sTable form (Khandegar *et al.*, 2013).

2.4.5 Cementation

Cementation is another precipitation method employing an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe (I) to ferrous Fe (II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner (Chen *et al.*, 2017).

2.4.6 Reverse osmosis and electro-dialysis

Reverse Osmosis is one of the finest methods of water filtration. This process allows the removal of all particles as small as ions from a solution. It is used to purify water and remove salts and other impurities in order to improve the colour, taste or properties of water. Reverse Osmosis uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it while rejecting other ions and contaminants from passing. This technology uses a process known as cross flow to allow the Reverse Osmosis membrane to continually clean itself. The membrane is put into a container (membrane housing) so pressure can be maintained on its surface. It is this pressure that supplies energy to force the water through the membrane, the higher the pressure, the larger the driving force and efficiency (Xiong *et al.*, 2019).

2.5 Adsorption Process and Mechanism

28

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Sorption encompasses both processes, while desorption is the reverse process (Adetokun *et al.*, 2018).

Adsorption offers significant advantages like low cost, availability, profitability, ease of operation and efficiency, in comparison with conventional methods (such as membrane filtration or ion exchange) especially from economic and environmental points of view. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy (Ofudje *et al.*, 2015).

In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting Physisorption or chemisorptions (Nemes and Bulgariu, 2016).

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases. Chemisorption on the other hand is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause Physisorption (Chen *et al.*, 2017).

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). Several models describing process of adsorption are: Freundlich isotherm, Langmuir isotherm, Brunauer Emmett-Tellery component (BET) isotherm etc (Ayawei *et al.*, 2017).

2.6 Adsorption Models

2.6.1 Adsorption isotherm

Adsorption isotherms are used for the description of how adsorbate will interact with adsorbent and are critical in optimizing the use of adsorbent. The correlation of experimental equilibrium data using either a theoretical or empirical equation is essential for adsorption data prediction.

2.6.1.1 Langmuir isotherm model

According to Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites which are interactions occurring between the adsorbed molecules homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and no interaction between the adsorbed molecules with variety of adsorbents (Ghosal *et al.*, 2017).

For Langmuir equation, it is written as:

$$1/q = 1/q_{max} + 1/(b.q_{max}) (C_f)$$
(2.1)

Where q_{max} and b are the Langmuir constants

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor R_L

$$R_{L} = \frac{1}{1 + K_{L}C_{o}},$$
(2.2)

Where K_L is Langmuir constant (mg g-1) and C_e is initial concentration of adsorbate (mg g-1). R_L values indicate the adsorption to be unfavorable when $R_L>1$, linear when $R_L=1$, favourable when $R_L<1$, and irreversible when $R_L=0$.

2.6.1.2 Freundlich isotherm model

Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents. This model, attributed to Freundlich, but was actually devised earlier by Boedecker and van Bemmelen (Ghosal *et al.*, 2017), is empirical and nonlinear in pressure:

$$q_e = K_f C^{1/n}$$
 (2.3)

$$Log q = log k + (l/n) log C_f$$
(2.4)

Whenever the graphical method is employed, the data are plotted as log q versus log p. The best straight line through the data has a slope of (l/n) and an intercept of log k. In general, k decreases with increasing temperature, while n increases with increasing temperature and approaches a value of 1 at high temperature. Where 1/n is the heterogeneity factor which is related to the capacity adsorbent and intensively depends on the physical and intensity of the adsorption. This model assumes that when the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly, the sorption energy exponentially decreases over the completion of the sorption Centre of the adsorbent (Okonkwo *et al.*, 2012).

Langmuir and Freundlich isotherm models are frequently used for describing the short term and mono-component adsorption of metal ions by different materials (Adetokun *et al.*, 2018).

2.6.1.3 Hill-Deboer model

The Hill-Deboer isotherm model describes a case where there is mobile adsorption as well as lateral interaction among adsorbed molecules, The linearized form of this isotherm equation is as follows

$$\ln\left[\frac{C_e\left(1-\theta\right)}{\theta}\right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2\theta}{RT},\tag{2.5}$$

Where K_1 is Hill-Deboer constant (Lmg-1) K_2 and is the energetic constant of the interaction between adsorbed molecules (KJmol⁻¹) (Hu *et al.*, 2021).

2.6.1.4 Fowler-Guggenheim model

Fowler-Guggenheim proposed this isotherm equation which takes into consideration the lateral interaction of the adsorbed molecules. The linear form of this isotherm model is as follows

$$\ln\left[\frac{C_e\left(1-\theta\right)}{\theta}\right] = -\ln K_{\rm FG} + \frac{2w\theta}{RT},\tag{2.6}$$

Where K_{FG} is Fowler-Guggenheim equilibrium constant (Lmg⁻¹), Θ is fractional coverage, R is universal gas constant (KJmol⁻¹K⁻¹), T is temperature (K), and ω is interaction energy between adsorbed molecules. This isotherm model is predicated on the fact that the heat of adsorption varies linearly with loading. Therefore, if the

interaction between adsorbed molecules is attractive, then the heat of adsorption will increase with loading because of increased interaction between adsorbed molecules as loading increases (i.e., ω = positive). However, if the interaction among adsorbed molecules is repulsive, then the heat of adsorption decreases with loading (i.e., ω = negative). But when ω =0 then there is no interaction between adsorbed molecules, and the Fowler-Guggenheim isotherm reduces to the Langmuir equation (Ayawei *et al.*, 2017).

2.6.1.5 Dubinin-Radushkevich isotherm

Dubinin-Radushkevich isotherm model is an empirical adsorption model that is generally applied to express adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces. This isotherm is only suitable for intermediate range of adsorbate concentrations because it exhibits unrealistic asymptotic behavior and does not predict Henry's laws at low pressure. The model is a semiempirical equation in which adsorption follows a pore filling mechanism. It presumes a multilayer character involving Van Der Waal's forces, applicable for physical adsorption processes, and is a fundamental equation that qualitatively describes the adsorption of gases and vapours on microporous sorbents. It is usually applied to differentiate between physical and chemical adsorption of metal ions. A distinguishing feature of the Dubinin-Radushkevich isotherm is the fact that it is temperature dependent; hence when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy, all suitable data can be obtained (Hu *et al., 2021*). Dubinin-Radushkevich isotherm is expressed as follows.

$$\ln q_e = \ln q_m - \beta E^2 \tag{2.7}$$

$$\epsilon = \operatorname{RT}\ln\left(1 + \frac{1}{C_e}\right) \tag{2.8}$$

Where ϵ is Polanyi potential, β is Dubinin-Radushkevich constant, R is gas constant (8.314 Jmol⁻¹ k⁻¹), T is absolute temperature, E and is mean adsorption energy.

2.6.1.6 Temkin isotherm

Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption of all molecules in the layer decreases linearly as a result of increase surface coverage. The Temkin isotherm is valid only for an intermediate range of ion concentrations (Chu, 2020). The linear form of Temkin isotherm model is given by the following

$$q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_e.$$
(2.9)

Where *b* is Temkin constant which is related to the heat of sorption (Jmol⁻¹) and K_T is Temkin isotherm constant (Lg⁻¹).

2.6.1.7 Flory-Huggins isotherm

Flory-Huggins isotherm describes the degree of surface coverage characteristics of the adsorbate on the adsorbent. The linear form of the Flory-Huggins equation is expressed as

$$\ln\left(\frac{\theta}{C_o}\right) = \ln K_{\rm FH} + n\ln\left(1 - \theta\right) \tag{2.10}$$

Where Θ is degree of surface coverage, *n* is number of adsorbate occupying adsorption sites, and K_{FH} is Flory-Huggins equilibrium constant (Lmol⁻¹). This isotherm model can

express the feasibility and spontaneity of an adsorption process. The equilibrium constant is used to calculate spontaneity Gibbs free energy as shown in the following expression

$$\Delta G^{o} = RT \ln \left(K_{\rm FH} \right) \tag{2.11}$$

Where ΔG° is standard free energy change, R is universal gas constant 8.314 Jmol⁻¹ K⁻¹, and T is absolute temperature (Hu *et al.*, 2021).

2.6.1.8 Harkin-Jura isotherm

Harkin-Jura isotherm model assumes the possibility of multilayer adsorption on the surface of absorbents having heterogeneous pore distribution (Mishra *et al.*, 2019). This model is expressed as follows

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e. \tag{2.12}$$

Where *A* and *B* are Harkin-Jura constants that can be obtained from plotting $1/q_e^2$ versus $logC_e$

2.6.1.9 Jovanovic isotherm

The Jovanovic model is predicated on the assumptions contained in the Langmuir model, but in addition the possibility of some mechanical contacts between the adsorbate and adsorbent (Chu, 2020). The linear form of the Jovanovic isotherm is expressed as follows.

$$\ln q_e = \ln q_{\max} - K_J C_e,\tag{2.13}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg g-1), q_{max} is maximum uptake of adsorbate obtained from the plot of lnq_e versus C_e , and K_j is the Jovanovic constant.

2.6.1.10 Elovich isotherm

The equation that defines this model is based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption; this implies a multilayer adsorption. The equation was first developed to describe the kinetics of chemisorption of gas onto solids (Hu *et al.*, 2021). The linear forms of the Elovich model are expressed as follows

$$\frac{q_e}{q_m} = K_E C_e e \frac{q_e}{q_m}$$
(2.14)

with the linear form expressed as follows

$$\ln \frac{q_e}{C_e} = \ln K_e q_m - \frac{q_e}{q_m}.$$
(2.15)

Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of $ln(q_e/C_e)$ versus q_e .

2.7 Adsorption Thermodynamic

Temperature is an important parameter for the sorption of metal ions related with the thermodynamics of the adsorption process. Generally, there are two common types, endothermic and exothermic sorption processes which are determined based on the increase or decrease in the temperature during adsorption. If the sorption increases with the increasing temperature, the sorption is an endothermic process whereas if the sorption decreases with the increasing temperature it is described as an exothermic
process. The equilibrium constant obtained from Langmuir equation at various temperatures is used to determine the thermodynamic parameters such as the enthalpy (H), free energy change (G) and entropy change (S) (Lunge *et al.*, 2014).

The adsorption of different heavy metals is quite different and the thermodynamic parameters of the metal ion sorption are dominated by the nature of metal ion, nature of sorbents, solution conditions, ionic strength and experimental conditions.

2.7.1 Factors affecting the adsorption of heavy metals

Various factors influence the adsorption capacity of potential adsorbents during the adsorption process. Previous researches have assumed that the efficiency of any adsorbent is strongly influenced by the physicochemical characteristics of the solutions such as pH, temperature, initial concentration, contact time and also adsorbent dose. A large portion of adsorption studies has been compiled to investigate the relationship of these parameters (Gong *et al.*, 2018).

2.7.1.1 Effect of pH

Adsorption of metal ions from wastewater is mainly influenced by the pH of the solution. pH can influence the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. In a particular pH range, most metal sorption is enhanced, increasing to a certain value followed by a reduction when further pH increases. The dependence of the metal uptake on pH can be associated with both the surface functional groups on the biomass' cell walls and also the metal chemistry of the solution The pH value of the medium affects the equilibrium of the system (Li *et al.*, 2013: Lunge *et al.*, 2014).

Where [A] and [AH], represent the concentration of deprotonated and protonated surface groups and the equilibrium constants p Ka resembled the carboxyl groups (Adetokun et al., 2018). The effect of pH in the metal ion uptake was investigated for the removal of Pb(II) ions using the polkan peel by Alnabriss (2018). The pH within the range of 2.0-8.0 was studied and the maximum adsorption occurred between 2.5 and 5.0, that was attributed to the dissociation of carboxylic acids at lower pH values which leads to the formation of carboxylate groups plus H⁺ and an increase of pH value adsorption process can be estimated from equilibrium from 2.0 to 5.0, giving the increased amount of metallic ion adsorbed. Meanwhile, pH higher than 5.0, was reported to have drastic decrease in the metallic uptake due to the hydrolysis of the metallic ion that takes place. The effect of pH on banana peel was also investigated by Oyekanmi et al., (2019). Increase in adsorption capacities of Cu (II) was reported from 0.7 mg/g to 1.76 mg/g with the increase in pH from pH 2 to pH 6, which was attributed to the availability of free ion at pH below 6. However, the adsorption capacity decreased after pH 6 to pH 12. This was further explained that at low pH, Cu ions compete with hydrogen ion for binding site on the adsorbent surface while at higher pH, Cu ions started to precipitate in the solution. The effect of pH was also studied by Mahapatra et al., (2020) in the range of 6-10. The microbe used in the process i.e. bacteria of Serratia Sp. ceased to grow in extreme acidic and extreme alkaline conditions. The percentage removal of phenol shows a decrease after the pH 7 and shows a maximum removal of 76 % at a pH between 6 and 7. This was attributed to the fact that phenol adsorption takes place mainly in its un-dissociated form as phenol has a pKa of 9.96 under which it remains in un-dissociated form. In the case of cyanide, the maximum removal was 96 % at pH 7 and then decreases in alkaline conditions. Since the pH is not reduced below 6, the pressure is maintained and there is no evolution of HCN. Since the pKa of cyanide is 9.39 therefore cyanide also shows the behavior of getting adsorbed in its undissociated form.

2.7.1.2 Effect of temperature

Depending on the temperature of the adsorbent used, temperature can affect the adsorption capacity of adsorbent. Temperature can change the adsorption equilibrium depending on the exothermic or endothermic nature of a process. Enthalpy, entropy and Gibbs free energy are such parameters that need to be determined before the spontaneity of the process can be inferred. Gibbs free energy (G°) is considered as the spontaneity indicator of a chemical reaction. The influence of temperature on the Kinetics and thermodynamics studies of methylene blue (MB) adsorption using corn-husk was investigated by Oana et al., (2013) at 298, 313, and 333 K, using a MB solution with 20 mg L⁻¹ initial concentration, and pH 6. It was reported that over time, it was observed that the necessary time for reaching equilibrium decreases from 80 minutes to 45 minutes with the increase of temperature, most of the dye being adsorbed in the first hour of the process. The adsorption capacity and the percentage of MB removal had decreased with the increase of temperature suggesting that adsorption of MB is an exothermic process. These results are economically advantageous because the MB 50 removal can be conducted at environmental temperature (25 °C) without additional costs for power generation.

2.7.1.3 Effect of contact time

The adsorption of metal ion by an adsorbent also depends on the interactions of functional groups between the solution and the surface of adsorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of solution and the adsorbent (Priya and Chandrajit 2014). However, specific time is needed to

maintain the equilibrium interactions to ensure that the adsorption process is complete. The effect of contact time on saw dust and neem bark for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions has been reported by Kumar et al., 2021. The experiment measures the effect of contact time under batch adsorption's initial concentration and pH of 25 mg/L and pH 5 for Zn(II) while 10 mg/L and pH 6 for Cd(II) under contact time varied from 0 to 5 h. it was reported that for the first 2 hours, the increased contact time enhanced the adsorption of both ions. However, the rapid adsorption initially affected the time needed to reach equilibrium. For saw dust, the equilibrium time was 3hr for both Zn (II) and Cd(II) adsorption while for neem bark, 3 and 4hr were recorded as time required to reach the equilibrium for the adsorption of Zn(II) and Cd(II), respectively. Hence, 4hrs contact time was established as an optimum contact time for future studies. Rao and Khatoon, (2017) also recorded the range of contact time varied from 1 to 180 min with a significant removal of different metal ions occurred during the first 20 min and no appreciable changes in terms of removal were noticed after 120 min. The adsorption of Cu(II), Cr(III), Ni(II) and Pb(II) ions was reported to be initially high probably due to the availability of the larger surface area of the sawdust for the adsorption of these ions. For all subsequent experiments, the equilibrium time was maintained at 120 min which was considered sufficient for the removal of different metal ions by Meranti sawdust.

2.7.1.4 Effect of initial concentration

Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases (Shaikh *et al.*, 2018). The Cr(VI)

adsorption on sawdust as adsorbent is significantly influenced by the initial concentration of the aqueous solutions as observed by Lui *et al.*, (2020). Results obtained show that the increase of the Cr(VI) concentration from 50 to 500 mg L-1 decreased the percentage removal from 99.9% to 89.9% due to limitations of active sites on the adsorbent which become saturated above a certain concentration. The adsorption capacity increased from 4.98 to 41.45 mg g-1 due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. The rapid adsorption of Cu(II) using watermelon shell after 20 min before it proceeds at a slower rate and attains saturation has been investigated (Uddin *et al.*, 2018). As the initial concentration of Cu(II) increased from 6, 10 and 20 ppm, the adsorption removal had decreased which was probably due to the fact that at lower concentration, almost all Cu(II) ions were adsorbed very quickly on the outer surface. However, further increase of the initial concentration of Cu(II) leads to the fast saturation of adsorbent.

2.7.1.5 Effect of adsorbent dose

Adsorbent dose is another parameter used to determine the capacity of adsorbent at a given concentration of the adsorbate. The effect of adsorbent dosage on bale tree (BT) leaf powder to adsorb Ni(II) from aqueous solutions has been investigated (Georgieva *et al.*, 2020).The effects of adsorbent dosage were varied from 5 to 30 g/L under room temperature (30°C) and with initial concentration at 10 mg/L. Result obtained from this study describes the adsorption of Ni(II) which increased rapidly when the dose of BT leaf powder was increased from 5 to 20 g/L, further explaining the large availability of the surface area at higher concentration of adsorbent. Any further addition of the

adsorbent beyond this would not cause any significant change in the adsorption due to the overlapping adsorption sites of adsorbent particles.

2.7.1.6 Effect of effluent flow rate

Effluent flow rate is another key parameter used in the study of adsorption kinetics in fixed bed adsorption. The effect of flow rate on almond shell adsorbent for the removal of Cr and Cu from tannery effluent has been investigated by Yahya *et al.*, (2020d), flow rates of 3.0, 6.0, and 9.0 ml/min were considered. Results obtained from the study describes the breakthrough time having an inverse relationship with flow rate. This was attributed to the rise in the rate of mass transfer which consequently leads to the increase in the quantity of metal ions adsorbed on to the mass transfer zone (unit bed height).

2.8 Desorption and Regeneration of Heavy Metals from Sorbent

The release of adsorbate from the surface of bio sorbents is termed as desorption. Desorption is an essential factor considered during determination of methods dependent on the principle of biosorption. Desorption activity is explained by the ratio between solid and liquid (S/L ratio) where the solid phase is the adsorbent on which heavy metals are adsorbed and the liquid phase is the desorbing eluent (Chatterjee and Abraham, 2019). Desorption helps in understanding the reusability of the biosorbents without any loss of effectiveness of the biosorbent. Also, desorption reduces the cost of the biosorption process due to the reuse of the sorbents. Different desorbents like acids, alkalis and alcohols are applied in removing the sorbates from the biosorbents. The procedure to accomplish desorption technique depends on the sorbate to a great extent. Solvents such as methanol, ethanol, NaOH solution can be used for desorption to regenerate the biosorbent used in adsorption of dyes (Debnath *et al.*, 2020). The desorbing eluent is chosen based on some dominant factors, which are efficient in

desorption, non-hazardous effect on the biosorbent, economic and non-polluting activity (Chatterjee and Abraham, 2019). However, it is noted that the contact between eluent and adsorbent is maintained for proper time duration because prolonged duration of contact might cause structural changes of the sorbents (Kumar *et al.*, 2021). The percentage of heavy metal desorption efficiency are determined following equations 2.2

%R

$$= \frac{C_o - C_i}{C_o} \times 100\%$$
 (2.16)

In the above equation, C_0 denotes the concentration of heavy metals (mg/L) attached to the adsorbent before desorption experiment and C_i is the heavy metals concentration (mg/L) in the adsorbent after the experimental analysis

$$q = \frac{\mathrm{VC}_f}{\mathrm{M}} \tag{2.17}$$

The q in the equation indicates the amount of heavy metal ions per unit adsorbent after desorption (mg/g),V denotes the volume of the desorbents used, M is the mass (mg) of the adsorbent taken for the study and C_f is the heavy metals ions concentration after the desorption (mg/L) (Kumar *et al.*, 2021).

$$\%Desorption = \frac{C_e.V_d}{Q_e.M_d} \times 100\%$$
(2.18)

In the above equation, C_e is the concentration of heavy metals in the desorbents (mg/g), V_d is the volume of the desorbents (L), Qe is the concentration of heavy metals on the adsorbent before desorption study (mg/L) and M_d is the mass of the heavy metals loaded adsorbent (g) (Liu *et al.*2020). The complete process of adsorption depends on the sorption, desorption and also the reusability of the sorbent. Regeneration of sorbents for their reutilization for a span of cycles requires non-hazardous desorbents. One of the

primary reasons for desorption activity is regeneration of the adsorption ability of the sorbent so that it can be reused. The regeneration efficiency highly depends on the pH of the desorbing eluent since removal of cations is inconsequential in lower pH or acidic solutions whereas basic solutions are incapable of recovering anions. Thus, to achieve maximum regeneration efficiency, a proper desorbing eluent must be chosen (Chatterjee and Abraham, 2019). Regeneration efficacy (RE%) of an adsorbent is calculated by equetion2.2d

% R

$$=\frac{A_r}{A_o} \times 100\% \tag{2.19}$$

The above equation indicates the adsorption capacity of the adsorbent post regeneration (mg/g) and the original adsorption capacity of the adsorbent (mg/g) respectively.

2.8.1 Desorbents used for heavy metals

Several researches have been carried out to evaluate the activity of inorganic and organic acids on sorbents. The sorbents were recycled and used to check the effectiveness after desorption process. Hydrochloric acid, nitric acid, sulfuric acids are a few common acids used for desorption of heavy metals from biosorbent. The activities of the acids on biosorbent are explained as follows:

2.8.1.1 Hydrochloric acid

Desorption of copper, zinc, cadmium and cobalt from bio char and commercial activated carbon have been attempted using hydrochloric acid. Using 6 M HCl for zinc ion sand 9.5 M for cadmium and copper ions resulted in release of 90%, 90% and 85%

of the respective metals and the adsorbing quality of the sorbent was unaffected after the desorption procedure with hydrochloric acid. The acidic desorbents protonates the surface of the biosorbent and thus results in desorption of the adsorbed heavy metal ions (Abdolali, 2017). 90.8% of lead was desorbed from lead adsorbed sulfonated expanded graphite sorbent using 0.1 M HCl (Jiao et al., 2017). 1.0 M HCl solution could remove 44.2% of cadmium ions from heavy metal loaded cellulose acetate membrane (Kamaruzaman et al., 2020).Copper and chromium adsorbed on biosorbent prepared using sawdust was successfully desorbed by 0.1 N hydrochloric acid (Witek-Krowiak, 2013).In case of cadmium removal from biosorbent obtained from algae Ecklonia maxima as well as waste of 'kelpak' which is a commercially available seaweed concentrate, hydrochloric acid is reported to be better desorbing eluent than sulfuric acid. Cadmium desorption occurs at a pH below 3which is the reason behind acids being suitable desorbents for the cadmium ions. Dilute concentration of HCl can increase the pH and thus are not efficient enough to break the complexes formed between metal ions and the biosorbent surface (Kumar et al., 2021). A series of heavy metals, such as, iron, aluminum, cadmium, zinc, nickel and lead were desorbed using 0.1 N HCl from modified fly ash sorbent, thus, confirming the efficacy of HCl as strong desorbing agent (Mishra et al., 2018).

2.8.1.2 Nitric acid

Nitric acid was proved to be the most efficient desorbing agent when compared to HCl and H_2SO_4 for desorption of copper, zinc, cadmium, and cobalt from biochar and activated carbon (Zhou *et al.*, 2021). The use of 0.1 M Nitric acid was capable of desorbing 85.7% lead ions from lead loaded sulfonated expanded graphite (Jiao *et al.*, 2017). The application of 0.1 M HCl was checked for desorbing cadmium, copper and lead from spent coffee ground sorbent. The adsorption capacity of the sorbent was not

affected by interaction with the nitric acid. Moreover, the reports showed that four consecutive adsorption-desorption cycles can be conducted using nitric acid as desorbing eluent. The excessive quantity of protons in nitric acid solution interacts with the sorbents and disrupts the bond between the sorbate and sorbent (Guzman *et al.*, 2016).

2.8.1.3 Sulfuric acid

Sulfuric acid has been considered as desorbing agent by various researchers. Adsorbent prepared using cellulose acetate with acetone and dimethyl formamide, named as cellulose acetate membrane has been able to adsorb copper and cadmium. The utilization of 1.0 M sulfuric acid as desorbents eluent showed that the inorganic acid could dislocate 32.1% of copper and 20.3% of cadmium. The sorbent was capable of being used for three cycles followed by regeneration using1.0 M sulfuric acid (Kamaruzaman *et al.*, 2020). However, sulfuric acid is not applicable for desorption of recovering lead from sorbents due to constitution and precipitation of lead sulfate.

2.9 Low Cost Adsorbents

Activated carbon has been a widely-used adsorbent in wastewater treatment all over the world. Inspite of its prolific use, activated carbon remains an expensive material, since the higher the quality of activated carbon, the greater its cost. Activated carbon also requires complex agents to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency (Yahya *et al.*, 2020b). Due to the problems mentioned previously, research interest has been shifted to the production of alternative adsorbents, especially those which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost. These include natural zeolite, ash, rice husk, peat, volcanic stones, bentonite and clinoptilolite for adsorption

of heavy metal ions (Lung et al., 2014). In particular, some natural materials, such as polysaccharides, clays, biomass, etc. that can remove pollutants from contaminated water at low cost has been widely researched around the world (Adetokun et al., 2018). Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial byproduct and natural material and due to its abundant availability, agricultural wastes such as peanut husk, rice husk, coconut shell, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems (Oana et al., 2013). Moreover the utilization of these waste materials as such directly or after some minor treatment as adsorbents is becoming vital concern because they represent unused resources and cause serious disposal problems. A growing number of studies have been carried out in recent years to evaluate the behavior of emerging adsorbents such as agricultural products and byproduct for emerging contaminants removal on the other hand industrial wastes, such as, fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry are currently being investigated as potential adsorbents for the removal of the emerging contaminants from wastewater (Mishra et al., 2019). Carbonized Corn Husk (CCH) and Activated Corn Husk (ACH) made out of corn husks and available as agricultural waste are investigated as viable materials for treatment of Pb, Cd, Cu, and Zn contained in industrial wastewater, at controlled pH. The results obtained from the batch experiments revealed a relative ability of the corn husk in removing some heavy metals at pH 7.

S/ n	Tittle	Modificatio n technique	Reagents	Res	ults	Autho r
1	Functionalize d Magnetic Nanoparticle s Supported on Activated	Co- precipitation method	FeCl ₃ .6H ₂ O and FeCl ₂ .4H ₂ O, ethanol–water mixture (4:1), 3- aminopropyl triethoxysilane (APTES), 10% succinic	Cr (VI)	80	Fatehi <i>et al.</i> , 2017

	Carbon for		anhydride, N,N			
	Adsorption		dimethylformamide (DMF)		90	
	of Cr(VI) Ion			Pb		
	from Saline			(II)		
	Solutions					
2	Adsorptive removal of Pb(II) by magnetic activated carbon incorporated with amino groups from aqueous	Co- condensatio n method	FeCl ₃ .6H ₂ O and FeSO ₄ .7H ₂ O, Alcohol- deionized water mixture (12:1), Ammonia, tetraethoxysilane,Aminopro pyl trimethoxisilane	Pb (II)	104. 2 mg/g	Fu <i>et</i> <i>al.,</i> 2016
	solutions					

Table 2.1 Previous work	s on functionalized	l adsorbents contd

S/ n	Tittle	Modificati on technique	Reagents	Results	Author	S/n
4	Magnetic iron oxide nanoparticles tea waste for arsenic remov	from Therma	al FeCl ₃ .6H ₂ O, M nt dimethylformat (DMF), magnet	N,N As mide (III tized)	98.4	Lunge <i>et al.</i> , 2014
5	Corn husk derived magnetized activated carbon for the removal of phenol and para- nitrophenol from	Thermal I treatment	FeCl3,dimethylforma mide (DMF), magnetized before carbonizaton at 250°C and 500°C	Phenol Pare Nitro- phenol	92 98	Mishr a <i>et</i> <i>al.</i> , 2019

aqueous	
solution	

6	Magnetic Activated Carbon Derived from biomass (Coconut shell) Waste by Concurrent Synthesis: Efficient Adsorbent for Toxic Dyes	Concurrent Synthesis	ferric chloride (FeCl ₃ .6H ₂ O), magnetized using three different ratios (1:1, 2:1, and 3:1) carbonization 700 ⁰ C	Methylene blue	98	Cazet ta <i>et</i> <i>al.</i> , 2016
7 Tab	Ultrasonic Pretreated Sludge Derived Magnetic Active Carbon for Cr(VI) Removal	Pyralyzed using ultrasonic- assisted impregnati on method	Fe(NO ₃) ₃ .9H ₂ O, pyrolyzed at 400, 600, 800 and 1000 ⁰ C,	Cr (VI)	203 mg/g	Gong <i>et al.</i> , 2018
	T:		nictionalized adsorber			
S/ n	Tittle	Modificati on	Reagents	Results	Author	S/n
		technique				
8	A novel magnetic biochar	Chemical co- precipitatio	Ferrous chloride and ferric chloride	Naphtalene	98.3	Chen <i>et al.</i> , 2011
	efficiently sorbs pollutants and phosphates	n		Phosphate	99.4	
9	Amine- functionali zed magnetic	in-situ co- precipitatio n method	Phosphoric acid, FeSO4, FeCl ₃ , NH ₃ .H ₂ O, epichlorohydrin	Ciprofloxac in Norfloxaci	Not availabl e	Peng <i>et al.,</i> 2018

activated carbon	ethylenediamine, triethylamine
adsorptive	thethylamine.
removal of	
ciprofloxac	
in and	
norfloxacin	
: A batch	
and fixed-	
bed	
column	
study	

2.10 Volume and Pore Size Distribution

Activated carbon is widely used adsorbent in wastewater treatment, especially in the removal of heavy metal ions due to its high specific surface area and affinity to metals. It is highly porous, therefore possessing very large surface area, which ranges from 300 to 1200 m^2/g (Phoon, 2013). The large surface area of the activated carbon contributes to the adsorption process itself, since there are more reactive sites for the adsorbates to bind on the surface of the activated carbon. Activated carbon can be manufactured from a variety of precursors via physical or chemical activation (Kameswara and Venkateswarlu, 2012). Physical activation is usually carried out in two steps: firstly, carbonization of raw materials is done in an inert atmosphere at a temperature below 700 °C, and the second step is the activation in the presence of steam, carbon dioxide, and/or air at temperatures between 800 and 1000 °C (Phoon, 2013). Chemical activation is generally carried out in one step, which consists of the impregnation of the raw material with a strong dehydrating agent, such as H₃PO₄, ZnCl₂, K₂CO₃, NaOH or KOH, and then heating the mixture to temperatures of 400 - 800 °C to simultaneously form and activate the carbon (Kameswara and Venkateswarlu, 2012). Chemical activation provides a few advantages over physical activation which include single step activation, low activation temperatures, shorter activation time, higher yields and better porous structure (Igwe and Abia, 2010). The chemical agents used are usually substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products (Nhapi et al., 2012). The disadvantage of chemical activation process is the need for an important washing step, which is time consuming due to number of washings required to completely remove the activation agent from the carbon (Balasubramanian et al., 2014). This process illustrated above makes its highly expensive and thus alternatives from available options became a necessity.

The use of chemically modified biomass for adsorption became a better alternative as the modification of the adsorbent provides more pore and thus binding space for adsorption to take place. The process involves impregnation as explained above with the exception of carbonization (Igwe and Abia, 2010). Overly high impregnation ration can also cause excessive reaction between the activating chemical and the lignocelulistic biomass thus hindering the formation of pores. It is also reported that the suitable range of carbon content in raw material, must be in between 50 - 80% so that the yield can be maintained at reasonable range (Okonwko et al., 2012). Besides the pore size of the corn husk biosorbent must be at least of meso pores level according to the IUPAC classification (Marsh and Reinoso, 2006; Kamil, 2014).

Table 2.2: IUPAC classification of pore size (2017)				
Classification of Pores	Pore diameter (nm)			
Macro pore	Larger than 50			
Meso pore	50 - 2			
Micro pore	Smaller than 2			
Super-micro pore	0.7 - 2			
Ultra-micro pore	0.7 - 0.4			

(0.04

2.11 Analytical Tools

The analysis carried out for the determination of the properties of an adsorbent and adsorption qualities varies with the type of adsorption process used (batch or continuous) and the adsorbate under study. For the determination of adsorbent initial properties, analysis like the FTIR, SEM-EDX, TGA, XRD and BET are carried out using the appropriate devices while analysis for the adsorbate intake containing heavy metal is carried out using the AAS equipment.

2.11.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy is a technique which is used to obtain an infrared spectrum of absorption and emission, photoconductivity or Raman scattering of a solid, liquid or gas (Okonwko *et al.*, 2012). An FT-IR spectrometer jointly collects high spectral resolution data over a wide spectral range. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. The global of any absorption spectroscopy (FT-IR, UV-V is spectroscopy etc.) is measured how well a sample absorbs light at each wavelength.

To turn the raw data into the desired result, a computer processing is required (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform hence the name, Fourier transform spectroscopy. The raw data is sometimes called an intergerogram (Okonwko *et al.*, 2012).

2.11.2 Scanning Electron Microscope (SEM)

Scanning electron microscope uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample (Adetokun *et al.*, 2018). In most applications, data are collected over a selected area of the surface of the sample and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure, and crystal orientations (Shaikh *et al.*, 2018).

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions this includes acquiring elemental maps or spot chemical analyses, discrimination of phases based on mean atomic number (commonly related to relative density), and compositional maps based on differences in trace element (typically transition metal and Rare Earth elements). The SEM is also widely used to identify phases based on qualitative chemical analysis and crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Back scattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors can be used to examine micro fabric and crystallographic orientation in many materials (Adetokun *et al.*, 2018).

2.11.3 Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy is a spectro analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the techniques is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples used in pharmacology, biophysics and toxicology research (Adetokun *et al.*, 2018).

The modern form of AAS was largely developed during the 1950s by a team of Australian chemists. They were led by Sir Alan Walsh at the common wealth scientific and industrial Research Organization (CSIRO), Division of Chemical Physics, in Melbourne, Australia. Atomic absorption spectrometry has many uses in different areas of chemistry such as Clinical analysis which involves Analyzing metals in biological fluids and tissues such as whole blood, plasma, urine, saliva, brain tissue, liver, muscle tissue, semen etc, pharmaceuticals uses in some pharmaceutical manufacturing processes, minute quantities of a catalyst that remain in the final drug product and in water analysis for its metal content (Oana *et al.*, 2013).

2.11.4 Branauer-Emmett-Teller (BET)

Branauer-Emmett-Teller theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The BET theory refers to multi-layer adsorption, and usually adopts non-corrosive gases (like nitrogen, Air, CO₂ etc.) as adsorbate to determine the surface area data. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each

adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is

$$\frac{1}{\nu[(P_o/P) - 1]} = \frac{c - 1}{c\nu_m} \left(\frac{P}{P_0}\right) + \frac{1}{C\nu_m}$$
(2.20)

Where p and p_o is the equilibrium an saturated pressures of adsorbate at the temperature of adsorption, v is the adsorbed gas quantity, v_m is to mono layer adsorbed gas quantity and c is the BET constant.

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area S_{total} and the specific surface area S_{BET} are given by

$$S_{total} = \frac{Nsv_m}{V}$$
 and $S_{BET} =$

$$\frac{S_{total}}{a}$$
(2.21)

Where V_m is in units of volume with is also the units of the molar volume of the adsorbate gas, N is Avogadro's number, S is the adsorption cross section of the adsorbing species, V is the molar volume of the adsorbate gas, and a is the mass of the solid sample or adsorbent.

The BET theory can be derived similar to the Langmuir theory, but by considering multilayered gas molecule adsorption, where it is not required for a layer to be completed before an upper layer formation starts. Furthermore, the authors made five assumptions.

1. Adsorption occur only on well-defined sites of the samples surface (one per molecule)

- 2. The only molecular interaction considered is the following one: a molecule can act as a single adsorption site for a molecule of the upper layer.
- 3. The uppermost molecule layer is in equilibrium with the gas phase, i.e. similar molecule adsorption and desorption rates.
- 4. The desorption is a kinetically limited process i.e. a heat of adsorption must be provided:
 - i. These phenomenon are homogeneous i.e. same heat of adsorption for a given molecular layer
 - ii. It is E_1 for the first layer, i.e. the heat of adsorption at the solid sample surface
 - iii. The other layers are assumed similar and can be represented as condensed species, i.e. liquid state. Hence, the hat of adsorption is E_L is equal to the heat of liquefaction.
- 5. At the saturation pressure, the molecule layer number tends to infinity (i.e. equivalent to the sample being surrounded by a liquid phase (Oana *et al.*, 2013).

2.12 **Proximate and Ultimate Analysis**

Conducting Proximate and Ultimate analysis in biosorption is also necessary because volatile matter and fixed carbon content are indicators of both carbonization degree and porosity development because during the carbonization stage, the porosity of char is formed through the release of volatile matter. Additionally, during the activation stage, steam consumes fixed carbon from the char's pore walls, widening them in the process, the limiting stage is represented by the steam adsorption on to a solid surface, which makes the distribution of fixed carbon and volatile matter determine the production of the activated carbons. (Uribe *et al.*, 2015). Ash content on the other hand does affect adsorption properties as it creates inactive sites. (Mendoza *et al.*, 2020)

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 Overview of Material and Methodology

This chapter outlines the materials, methods and techniques used in this research. It outlines all the analytical techniques and instruments used in material pretreatment, modifications characterization effluent evaluation and synthesis.

3.2 Materials

Materials needed for this project includes the raw material (precursor) for the adsorbent which is corn husk. This biomass is considered because of its relative availability in commercial quantity. Other materials needed are the chemicals required for analyzing, treating and modifying the adsorbent as well as the effluent solution for the adsorption process. The materials needed are tabulated in Table 3.1



Plate I: corn husk waste

S/No	Material/reagents	Manufacturer	Source
1	Corn husk		Road side corn roasters
			within Minna town
2	HNO ₃	Central drug house (p)	Panlac chemical stores
		110002 new Delhi India	Minna
4	Epichlorohydrin	Burgodine nad Co.	Chemistry laboratory, FUT
		India	Minna
5	N,N-	Kermel (UN No. 2265)	Chemistry laboratory, FUT
	dimethylformamide		Minna
6	Ethylenediamine	BDH chemicals Ltd	WAFT laboratory, FUT

Table 3.1: List of materials and reagents used

		England (28021)	Minna
7	Triethylamine	BDH chemicals Ltd	Panlac chemical stores
		England (27039)	Minna
8	Pyridine	BDH chemicals Ltd	Chemistry laboratory, FUT
		England (29707)	Minna
9	Ethanol	Kermel UN No. (1028)	Panlac chemical stores
			Minna
10	Distilled water		WAFT laboratory, FUT
			Minna
12	Sample bottles		Panlac chemical stores
			Minna
13	Glass wares		Chemical Engineering
			laboratories

3.3 List of Equipment Required

The equipment used in this study were generally for sample analysis and characterization. The equipment used for analysis were operated optimum conditions to guarantee excellent results with high accuracy and reliability. Table 3.2 shows the list of equipment used in this project.

S/No	Equipment	Model	Source
1	Weighing scale	Adventure – AR223CN	Chemical Engineering lab FUT Minna
2	Drying oven	Gallenkamp (OEF/021/10)	WAFT laboratory FUT Minna
3	Electric Blender	Marlex Exeller	Domestic blender
4	Sieves	BSS (ASTM-IS460)	Chemical Engineering lab FUT Minna
5	Magnetic stirrer	PEC medical (USA 85-2)	WAFT laboratory FUT Minna

Table 3.2. Lists of equipment used

6	Furnace	Gallenkamp (IIC106B, Impact)	WAFT laboratory FUT Minna
7	Scanning electron microscope (SEM- EDS)	PerkinElmer (634-BSS21)	Allschoolab scientific, lagos
8	Fourier transform infrared (FTIR)	Varian 660 MidIR Dual MCT/DTGS Bundle with ATR	ABUAD University Ado-ekiti
9	Atomic Absorption Spectrophotometer (AAS)	PerkinElmer (051-AV12)	Allschoolab scientific, lagos
10	Water bath shaker	AlabTech (LSB-0455)	Chemical Engineering lab FUT Minna
11	Thermo-gravimetric Analysis (TGA)	PerkinElmer	Step B laboratory, FUT Minna
12	Branauer-Emmett- Teller analysis (BET)	Quantachrone Novawin	Step B laboratory, FUT Minna

3.4 Preparation of Raw Materials

3.4.1 Adsorbent preparation

Corn husk was massively collected from corn roasters within Minna town in Niger State. After collecting sufficient husk of approximately 10 kg, they were first de-stoned then separated from all physical impurities including the tassels. The husk was further cut into tiny pieces and washed thoroughly with tap water to remove any form of dirt on the surface of the husk, then washed with distilled water, the wetted corn husk were sun dried to remove excess water from the husk and then oven dried at 60°C over night to remove any residual moisture.

The dried maize husk was crushed into smaller particles sizes using electric blender (Marlex Exeller). The resulting powdered sample was then segregated using a vibration

shaker of mesh sizes 500 the sample was kept in an



 μ m, 300 μ m and 250 μ m. air tight container for further



use. Plate IIa, IIb and IIc shows the corn husk after crushing and segregation into desired particles sizes.



Plate II A: Dried, B: Crushed (<500 µm,) and C: Segregated corn husk (250 µm)

3.4.2 Proximate analysis

The proximate analysis of corn husk was conducted to determine moisture content, ash content, volatile matter and fixed carbon.

3.4.2.1 Moisture content

The Moisture content (MC) of the dried maize husk was calculated as a percentage of "as received" or total mass of sample using the expression

$$\frac{M_{\text{oven dried}}}{M_{\text{as recieved}}} \times 100\%$$
(3.1)

3.4.2.2 Ash content

The Ash content (AC) of the sample was determined according to American Society for testing and materials (ASTM D 2974-8) by igniting the oven-dried sample from the moisture content determination in a furnace while the temperature gradually rose from room temperature to 550 0 C for 2 hrs. The substance remaining after ignition was the ash. The ash content was expressed as a percentage of the mass of the oven-dried sample

$$\frac{M_{ash}}{M_{oven dried}} \times 100\%$$
 3.2

3.4.2.3 Volatile organic carbon

The volatile organic carbon (VOC) was obtained by heating 5 gram of the sample in a furnace at 950 0 C for 7 minutes. The sample was then cooled in a desiccator and was reweight, the percentage VOC was determined thus

$$\frac{M_{heated}}{M_{raw}} \times 100\%$$
 3.3

3.4.2.4 Fixed carbon

The fixed carbon (FC) was determined by subtracting the various vales of MC, AC, and VOC from 100

3.4.2.5 Acid pretreatment

Acid pretreatment was used in this study as described by Fu *et al.*, 2016. Due to low temperature requirement and ability to obtain enhanced porous structure in the acid treated adsorbent. The treatment agent used is nitric acid (NHO₃). This organic acid was chosen because the results of using it showed better pore formation in the corn husk as compared to others (Mishra *et al.*, 2019; Paulguin *et al.*, 2018; Fatehi *et al.*, 2017). 20 g of 250 μ m sample size was mixed in a plastic basin containing 2% v/v nitric acid and stirred with a glass rod until a homogenous mixture was achieved. The mixture was allowed to settle for 18 hours and then sieved thereafter. The resultant sludge was thoroughly washed with distilled water and dried at 60 ^oC for 12 hrs. The dried sludge was crushed into 250 µm sample size and stored in an air tight container for further use. This process is shown in plate III



Plate III: Raw corn husk acid pretreatment

3.4.3 Adsorbent modification

3.4.3.1 Amination reaction

To synthesis an amine functionalized corn husk (AF-CH), the procedure described by Peng *et al.* (2017) was used with some modifications. The intermediate reaction was made by mixing 20 mL epichlorohydrin, 25 mL N, N-dimethylformamide and 11 mL ethylenediamine in a 250 mL round bottom flask at 80 °C on a rotary magnetic stirrer (IKA RV10) at 100 rpm for 60 min, 25 mL of trimethylamine was added to the solution afterwards and stirred for another 90 min. At the last step of the adsorbent synthetic protocol, 20 mL of pyridine (as the catalyzer) and 40 g treated corn husk was added to the mixture and stirred at 90 °C for yet another 90 min. After the reaction was completed, the resulting mixture was filtered and washed with 500 ml of ethanol (50%) and 2 liters of distilled water and then dried at 75 °C for 6 hrs. the resulting end product was allowed to cool to room temperature by keeping it inside a desiccator. The structural synthetic pathway is illustrated below



Ghadiri *et al.*, (2020)

Figure 3.1: Synthesis pathway for CHP functionalization through amination reaction

3.4.3.2 Corn husk based activation carbon

The result of the Thermo gravimetric analysis (TGA) obtained was considered in the choice of activation temperature range of 300, 400 and 500 ^oC. The cooled adsorbent was heat-treated at these various temperatures in a furnace (IIC106B, Impact) for 1 h., the resulting activated carbon was allowed to cool to room temperature in a desiccator before storing in an air tight container for further use. Plate 3.4 shows the final activated carbon obtained.



Plate IV: Functionalized corn husk based activated carbon

3.4.4 Adsorbent characterization

Characterization of the functionalized corn husk based activated carbon was carried out to determine the functional groups present in the raw and modified corn husk adsorbent using FTIR, the pore volume and surface area of the raw and modified corn husk was also determined through BET analysis, furthermore the surface morphology of the adsorbents (both modified and raw) was determined through SEM-EDS analysis.

3.4.5 Effluent collection and analysis

Effluent wastewater was collected from a local battery recycling drain at Keteren Gwari in Minna and was analyzed for physiochemical properties, the effluent as received from point source was taken to the laboratory for quantitative analysis of common heavy metal pollutants in battery processing companies such as Lead, Iron, Copper, Nickel, chromium, Cadmium, and Zinc.

3.4.6 Adsorption test

3.4.6.1 Batch adsorption study

Batch adsorption study was carried out to study the effect of five different variables on the removal efficiency, the variables which include contact time, effluent pH, initial concentration, adsorbent dosage and temperature were all varied as listed in Table 3.3 and at a constant agitation rate of 150 rpm and the resulting percentage removal was recorded against each experimental run. Briefly, 50 mL of various effluent initial concentrations were measured into a conical flask and various adsorbent dosages ware measured in correspondingly, the pH of the solution was adjusted to the corresponding pH values on the experimental runs and the beakers were placed on a water bath shaker while the agitation rate was set to 150 rpm, the resulting percentage removal and amount adsorbed were calculated using equation 3.4 and 3.5 respectively.

$$\%R = \frac{C_O - C_F}{C_O} \times 100\%$$
 3.4

$$q = \frac{C_O - C_F}{M} \times V \tag{3.5}$$

Considering the analysis result of the local battery recycling wastewater collected, the initial concentrations of heavy metal was considered and varied using a dilution factor of 10 to 100 % effluent concentration. a total of 50 experimental runs with constant working parameters of 100 % effluent concentration (Pb: 160mg/L, Cu: 122 mg/L and Ni: 100 mg/L), contact time of 60 min, adsorbent dosage of 1 g, pH of 2 and temperature of 30 °C was used by varying one parameter at a time while keeping others constant. The pH range of 2 to 11 was also considered from the physiochemical properties of the analyzed wastewater. The choice of time, temperature and dosage ranges was based on past literatures

Runs	Conce	ntration	(mg/L)	Time (min)	Dosage (g)	Ph	Temperature (°C)
	DI	G					
1	Pb	Cu	<u>N1</u>	<u></u>	1.0		20
1	16	12	10	60	1.0	2	30
2	32	24	20	60	1.0	2	30
3	48	36	30	60	1.0	2	30
4	64	48	40	60	1.0	2	30
5	80	60	50	60	1.0	2	30
6	96	72	60	60	1.0	2	30
7	112	84	70	60	1.0	2	30
8	128	96	80	60	1.0	2	30
9	144	108	90	60	1.0	2	30
10	160	122	100	30	1.0	2	30
11	160	122	100	5	1.0	2	30
12	160	122	100	20	1.0	2	30
13	160	122	100	35	1.0	2	30
14	160	122	100	50	1.0	2	30
15	160	122	100	65	1.0	2	30
16	160	122	100	80	1.0	2	30
17	160	122	100	95	1.0	2	30
18	160	122	100	110	1.0	2	30
19	160	122	100	125	1.0	2	30
20	160	122	100	140	1.0	2	30
21	160	122	100	60	0.5	2	30
22	160	122	100	60	1.0	2	30
23	160	122	100	60	1.5	2	30
24	160	122	100	60	2.0	2	30
25	160	122	100	60	2.5	2	30
26	160	122	100	60	3.0	$\overline{2}$	30
27	160	122	100	60	3.5	$\overline{2}$	30
28	160	122	100	60	4.0	$\frac{1}{2}$	30
29	160	122	100	60	4 5	$\frac{1}{2}$	30
30	160	122	100	60	5.0	$\frac{1}{2}$	30
31	160	122	100	60	1.0	$\frac{1}{2}$	30
32	160	122	100	60	1.0	3	30
33	160	122	100	60	1.0	Δ	30
34	160	122	100	60	1.0	5	30
35	160	122	100	60	1.0	6	30
36	160	122	100	60	1.0	7	30
30	160	122	100	60	1.0	/ 8	30
20	160	122	100	60	1.0	0	30
20	160	122	100	60	1.0	7 10	20
37	100	$1 \angle \angle$	100	00	1.0	10	30

Table 3.3: Experimental variable

Table 3.3: Experimental variable contd.

Runs		Concentration (mg/L)		Time	Dosage (g)	Ph	Temperature
	Pb	Cu	Ni	(min)			(°C)
40	160	122	100	60	1.0	11	30
41	160	122	100	60	1.0	2	25

42	160	122	100	60	1.0	2	30	
43	160	122	100	60	1.0	2	35	
44	160	122	100	60	1.0	2	40	
45	160	122	100	60	1.0	2	45	
46	160	122	100	60	1.0	2	50	
47	160	122	100	60	1.0	2	55	
48	160	122	100	60	1.0	2	60	
49	160	122	100	60	1.0	2	65	
50	160	122	100	60	1.0	2	70	

3.4.6.2 Desorption study

Desorption experiments was carried out as described by Adetokun *et al.*, 2018. The used F-CHAC was collected after filtering out the treated effluent and was weighed, the known weight of used F-CHAC was added to 50 ml HCl (0.1M) and was kept in a shaker for 3 hrs. After the incubation period, the reaction mixture was sieved and the filtrate was subjected to the estimation of Lead, cupper and nickel ion concentration using AAS, the residue containing desorbed F-CHAC was dried, weighed and subjected to fresh bio-sorption studies. This process was repeated 5 times at a constant pH, temperature, concentrations and time of 2, 30 °C, 100 % and 60 min respectively. Subsequent desorption studies were carried out and the percentage of heavy metal desorption efficiency, amount of heavy metal ions per unit adsorbent after desorption (mg/g) and the regeneration efficacy (RE %) were determined thereafter.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 **Collection of Result and Interpretations**

Proximate analysis 4.1.1

The results of proximate analysis of raw corn husk shows the presence of various constituent in in distinguished percentages, from Table 4.1, the fixed carbon constitute the highest percentage with over 50%, this implies that corn husk has high carbon content and hence is a good precursor for activated carbon, the presence of significant amount of volatile organic compounds also indicates the availability of high pore space, this is because the VOCs degrade at high activation temperature to pave way for pore formations. This result is in close agreement with the findings of Minaret et al., (2016) and Mishra et al., (2019) where 43.91 and 52.89 % of fixed carbon in raw corn husk were reported respectively.

S/N	Parameters	Values (%)
1	Moisture Content	12.50
2	Ash content	11.67
3	Volatile Organic Compounds (VOC)	20.84
4	Fixed carbon	54.99

Thermo Gravimetric analysis 4.1.2

The TGA analysis result shows a gradual loss of weigh as the sample was heated to a temperature of 300 °C, a spontaneous weight lost was observed afterword until it reaches a temperature of 500 °C, finally there was insignificant weight lost at temperature above 500 °C which can be observed from Figure 4.1, this implies that the sample is thermally stable at temperatures below 300 °C and can be thermally activated at a temperature of up to 500 °C, this is also in line with the result obtained by Fu et al., 2017



Figure 4.1: TGA Analysis of Raw corn husk

4.1.3 Thermal activation

The adsorbent which was thermally activated at three different temperatures shows varieties in the yield of the activated carbon formed, from Table 4.2, the activated carbon formed at a temperature of 300 $^{\circ}$ C tends to have higher yield which could be as a result of gradual heating that lead to gradual degradation of the VOCs and less ash formation. The activated carbon at 500 $^{\circ}$ C however shows lesser yield due to high heating rate and uneven supply of heat across the adsorbent surface, this result is similar to the findings of Tural *et al.*, (2018).

 Table 4.2: Thermal activation of F-CHAC

Temperature (°C)	300	400	500
Yield (%)	58	32	26

4.1.4 Effluent analysis

The analysis of wastewater collected from local battery recycling drains as presented in Table 4.3 shows the presence of various heavy metals in extreme concentrations, metals like Pb, Cu, Ni, Cr, Zn and Fe are present at concentrations above 10 mg/L with Pb having the highest concentration of 160 mg/L, the presence of these metals were expected as the recycling process involved the replacement of damaged cells which are made up of these metals and spent electrolytes which consist of dissolved metals and acids. The pH of the solution also indicates that the effluent is very acidic suggesting the presence of spent H₂SO₄ or HCl electrolytes. The values of BOD, COD and DO and TOC also indicate the presence of organic impurities and suggest the need to treat the effluent

S/N	Parameters	Analytical Values
1	BOD (mg/L)	18
2	COD (mg/L)	880
3	TOC (mg/L)	0.070
4	DO (mg/L)	32
5	pH	2.04
6	Cu (mg/L)	122.42
7	Pb (mg/L)	160.22
8	Ni (mg/L)	100.30
9	Cr (mg/L)	48.68
10	Zn (mg/L)	50.35
11	Fe (mg/L)	18.80

Table 4.3: preliminary effluent analysis

4.2 Adsorbent Characterization

4.2.1 Functional group composition

Fourier transform infrared spectral analysis carried out was aimed at identifying the presence of various functional groups in the adsorbent before and after modification. The functional groups which were recorded by the FT-IR includes the O-H stretch, C-H stretch, C=O stretch, C-Br stretch, C-O stretch, C-C stretch, C=C stretch and the N-H stretch as shown in Table.4.4. Figure 4.2a shows the FT-IR spectra of freshly prepared corn husk with an intense peak at 3862.72 cm⁻¹ which can be attributed to the stretching of O-H group due to inter and intra molecular hydrogen bonding such as alcohols or phenols (Madhu *et al.*, 2014). Another intense peak observed at 3796.52 cm⁻¹ can be

associated with C–H asymmetric stretching vibration of the CH₂ group (Pachathu *et al.*, 2016). The C-H bond of methoxy groups was noticed at a broad peak 3441.30 cm⁻¹ (El-Sakhawi *et al.*, 2018). An intense peak at 2780.61 cm⁻¹ was attributed to the C-H associated with alkynes and aromatics (Ali *et al*, 2014). An intense peak at 2398.06 cm⁻¹ was attributed to the C=O stretching vibrations of caboxylics while the steep peaks observed around 1630.29 to 1398.26 cm⁻¹ corresponded to the C-C stretching, and C-O asymmetric stretch which might be attributed to the presence of aromatic or olefinic or (Lin *et al.*, 2019). The intense peaks observed around 1003.01 to 898.34 cm⁻¹ corresponded to the C-Br Stretching vibration and C-O stretching of alcohol or carboxylic acid (Indha *et al.*, 2016).

The FT-IR spectrum of the modified adsorbent shown in Figure 4.2b reveals the peaks at 3850.13, 3632.07, 3450.53, 2389.63, 2128.13, 956.10, and 602.54 cm⁻¹ which were attributed to the O-H stretching vibration, C–H asymmetric stretching vibration of the connection of the in CH₂ group, C–H stretching vibration, C=O stretching vibrations, and C-Br Stretching vibration respectively. The presence of emerging intense peaks at 1390.27 and 1173.55 cm⁻¹ were attributed to the N–H bending vibration and C=O stretching of aldehydes and ketones which originates from the functionalization of the adsorbent. The corresponding increase or decrease in absorbance can be attributed to the emergence or disappearance of other functional groups which can be as a result of chemical modification and thermal treatment which degrades some volatile compounds and introduces other compounds as end product of thermal degradation. This result is in close agreement with the observation of Rashid *et al.*, (2019) while studying the use of naturally functionalized pumpkin peels for the decolourization of methylene blue. Table 4.4 shows comparison of FT-IR peaks and band representations of the freshly prepared and modified adsorbent.
			peaks and be	ind positions	
S/N	F-CHAC Peak (cm ⁻	F-CHP-AC Absorbance	CHP Peak (cm ⁻	CHP Absorbance	Assignment
1	3850.13	0.0571	3862.72	0.0260	O-H stretching vibration
2	3632.07	0.0362	3796.52	0.0423	C–H asymmetric stretching vibration of the connection of the in CH ₂ group
3	3450.53	1.1707	3441.30	0.3979	C–H symmetric stretching vibration of the connection of the in CH ₂ group
4	2389.63	0.0499	2780.61	0.0744	C–H stretching vibration
5	2128.13	0.0560	2693.61	0.0555	C=O stretching vibrations
6	1728.27	0.3132	2398.06	0.0171	C=O stretching vibrations
7	1390.27	0.0599	1630.29	0.1342	N–H bending vibration
8	-	-	1400.01	0.0560	C=O stretching of aldehydes and ketones
9	1173.55	0.0901	-	-	C-H Stretching vibration
10	1398.26	0.0754	-	-	C–C and C–N stretching vibrations
11	956.10	0.0714	-	-	C-H Stretching vibration
12	-	-	1098.77	0.0592	C-O Stretching vibration
13	-	-	1003.01	0.0486	C-O Stretching vibration
14	-	-	898.34	0.0359	C-H Stretching vibration
15	602.54	0.1184	500.06	0.0560	C-Br Stretching vibration

 Table 4.4: Comparison of FTIR peaks and band positions



Figure 4.2a: FT-IR Result of raw corn husk



Figure 4.2a: FT-IR Result of F-CHAC

4.2.2 Surface morphology

The results of SEM obtained shows actual pore structure of the adsorbent before and after modification, from Figure 4.3a, the presence of agglomerations were observed across the raw adsorbent surface, these were attributed to the presence of clogged pore sites. The volatile organic compounds and impurities which are present in the raw husk

are likely responsible for the packed or agglomerated pores. From Figures 4.3b, the presence of numerous pores were observed in the adsorbent after undergoing several modification, this was attributed to the formation of extra pores when the adsorbent was subjected to chemical treatment which lead to the corrosion of several blockages on the surface of the adsorbent and high temperature which also lead to formation of pores as the volatile organic compounds on the raw corn husk degrades. This is also an evidence to show that there is a transformation of the adsorbent from mere agglomerate to a highly porous structure with abundant binding sites. The energy dispersive spectroscopy of the adsorbent obtained in Figure 4.3c and 4.3d also shows the presence of numerous elemental compositions in the fresh and modified husk, the presence of new components (Nitrogen) in the functionalized husk (4.3d) was attributed to the amination reaction. The presence of Carbon, Hydrogen, Oxygen and Nitrogen in high percentages shows the availability of functional groups related to such elements on the surface of the adsorbent which is considered as a significant factor that aids in heavy metal binding. Fu et al., (2016) observed similar change in morphology after functionalizing magnetized activated carbon with amino groups.



Figure 4.3 a: morphology of raw corn husk, b: morphology of F-CHAC



4.2.3 Surface area and pore volume

The results of BET analysis for modified and unmodified corn husk adsorbent show the presence of large surface area and at various degrees. From Table 4.5, it shows that unmodified corn husk which has an initial surface area of 92.1 m²/g has increased by a very significant factor (more than 400%) after it was modified, this could be attributed to the increased porosity on the modified husk surface which is as a result of the chemical and thermal treatment it went through. This was further compare with previous research as shown in Table 4.5.

Adsorbent	Surface area (m^2/g)	References	
Raw Corn husk	92.11	This study	
F-CHAC	442.70	This study	
Pumpkin peels	360	Rashid <i>et al.</i> , (2019)	
Magnetic functionalized activated carbon	48.9	Fu <i>et al.</i> , (2016)	
Magnetic Nano- particles	432	Fatehi <i>et al.</i> , (2017)	
Wild pods Activated carbon	427.531	Adetokun <i>et al.,</i> 2018	

Table 4.5: Comparison of BET analysis result with literature

4.3 Adsorption Studies

The adsorption studies was carried out to study the effect of five parameters (concentration, temperature, dosage, time and pH) on the removal efficiency of functionalized corn husk derived activated carbon. This is further discussed.

4.3.1 Effect of contact time

The influence of contact time is an essential factor for the determination of adsorption efficiency as it establishes the time for sorbent-sorbate equilibrium. The contact time for adsorption studies on F-CHAC for the removal of selected heavy metals from battery recycling process wastewater was between for 5 to 140 min as shown in Figure 4.4, in this study, more than 38 % removal for lead and copper took place within the first 5 min of contact time which accounts for almost 50 % of the removal efficiency. The maximum percentage removal of the pollutants which justify the equilibrium time for

Pb, Cu, and Ni ions was 80, 79 and 87 % and at an optimum time of 95, 125 and 125 min respectively. The rapid adsorption of these pollutants before equilibrium time could be attributed to the availability of large and vacant active sites on the activated carbon surfaces. The gradual reduction in the rate of removal as it approaches equilibrium could be as a result of the saturation of the adsorbent active sites and the weakening of the binding force as a result of reduced sorbate concentration. This is similar to the findings of Fatehi *et al.* (2017) on the use of Functionalized Magnetic Nanoparticles Supported on Activated Carbon for Adsorption of Pb(II) and Cr(VI) Ions from Saline Solutions. They observed that initial rapid rate of adsorption was as a result of abundant sites on the surface of the functionalized activated carbon. It was also observed from Figure 4.5 that the removal of heavy metals from local battery recycling wastewater is in the order of Ni>Pb>Cu. Ni ion had highest percentage removal of 87 % and this behavior could be associated to ionic radii of the interested metal ions in the wastewater since metals with smaller ionic radius have more tendency to be adsorbed by the least available pores (Mustapha *et al.*, 2021).





Figure 4.4: Effect of contact time on the adsorptive removal of Pb, Cu, and Ni

4.3.2 Effect of adsorbent dosage

The adsorbent dosage is also a significant parameter in the removal of pollutants in wastewater. The effect of adsorbent dosage which ranges from 0.5 to 5 g on the removal of Pb, Cu, and Ni ions from Local battery recycling wastewater is presented in Figure 4.5. The removal percentage was observed to have increased with increasing F-CHAC dosage. The removal efficiencies of Pb, Cu and Ni ions increased from 41 to 99.36 %, 36 to 97.95 % and 38 to 95.92 % respectively at a dosage of 3 g, this implies optimum amount of F-CHAC needed to achieve equilibrium for the three metals. The trends as shown in Figure 4.6 could be attributed to slow adsorption rate at lower adsorbentadsorbate interface while the increase in percentage removal at higher dosages and fast equilibrium could be attributed to abundance of sorption sites as a result of wider surface area. Pb(II) with the highest electronegativity (2.33) removed more than Cu(II) (1.90) and Ni(II) 1.91). Thus, the adsorption efficiency of the heavy metals followed this order: Pb > Ni > Cu. This implies that the higher the electronegativity, the faster the rate of diffusion and removal efficiency. This is in agreement with the reports of Egbosiuba et al. (2020) and Mustapha et al. (2021). This however did not follow the trend of report by Onsinka (2017) because the author emphasized that the differences in adsorption rate was based on ionic radii which suggest that small ionic radii usually induce fast on the sorption site.



Figure 4.5: Effect of adsorbent dosage on the adsorptive removal of Pb, Cu, and Ni

4.3.3 Effect of temperature

Temperature affects the equilibrium capacity of adsorbent and also enhances diffusion rate of adsorbate across the external boundary and internal pores of adsorbent particles (Miyah *et al.*, 2018). The effect of temperature on the removal of Pb, Cu, and Ni at temperature range of 28 to 70 ^oC was investigated and presented in Figure 4.6. It was observed that adsorption of heavy metals increased with temperature and a significant increase was observed for temperatures up to 40 ^oC and this could be due to increase mobility of the adsorbate onto the active sites of the adsorbent at higher temperatures. However, the magnitude of such increase continue to decline as temperature is increased above 45 ^oC, this is because with increasing temperature, the attractive forces between biomass surface and metal ions are weaken and the sorption decreases, the thickness of the boundary layers are also reduced at higher temperatures hence the tendency for desorption of the already adsorbed metals suggesting further reaction as exothermic. Similar observation was reported by Horshfall and Spiff (2015) while studying the effect of temperature on the adsorptive removal of Pb and Cd ions from aqueous solution.



Figure 4.6: Effect of temperature on the adsorptive removal of Pb, Cu, and Ni

4.3.4 Effect of concentration

The effects of the initial adsorbate concentration were studied. 1 g of F-CHAC was used for all concentrations of Pb, Cu and Ni. The initial concentrations of the adsorbate were determine using a dilution rate of 10 % at a pH of 2 and a temperature of 30 °C. The adsorption behavior of the adsorbent at different initial concentrations is shown in Figure.4.7. The result shows that the adsorption percentage of all the metals tends to decrease with increasing initial concentration. The maximum adsorption of Pb, Cu and Ni was observed at the lowest initial concentrations of 16, 12 and 10 mg/L respectively. The maximum adsorption removal of Pb, Cu and Ni was found to be 94.8 %, 99.7 % and 99.8 % respectively. However, on increasing the initial concentrations of the metals, there was a sharp decrease in adsorption percentage, and the lowest removal percentage was observed at 100 % concentrations (Pb:160 mg/L, Cu:122.2 mg/L, and Ni:100 mg/L). This is because at lower concentrations, the number of adsorbate molecules was less than the number of adsorbent molecules providing a high surface area for adsorption. However, on increasing the initial adsorbate concentration the number of adsorbate molecules exceeded the number of adsorbent molecules, resulting in insufficient surface area for adsorption, and decreasing the adsorption percentage. Similar result was obtained by Adetokun *et al.*, (2018).



Figure 4.7: Effect of concentration on the adsorptive removal of Pb, Cu, and Ni

4.3.5 Effect of solution pH

The solution pH is an important parameter that determines the rate of adsorption, for the adsorption of heavy metal ions from local battery recycling wastewater, an increase in pH from acidic medium (pH 2) towards neutral (pH 7) lead to a corresponding increase in the rate of adsorption. At plateau values of pH 4, 5 and 6, a further increase in pH did not significantly affect the rate of adsorption of Pb, Cu and Ni respectively. This trend continued as the process moves through the basic regime until pH 8 were a decrease in adsorption rate was observed for all the heavy metals. The decrease in removal efficiency continued throughout. Since the solution pH has an impact on the solubility of metal ions, concentration of counter ions on the functional groups and the degree of adsorbent ionization. Pb, Cu and Ni can be present in several species (⁺, (OH)⁺, (OH)₂⁰ and (OH)₃⁻) depending on the solution pH. In the case of higher pH values (>7), several species with deferent charges including (OH)⁺ and (OH)₂⁰ are commonly found thus adsorption of the heavy metals may occur as a result of simultaneous precipitation of

 $(OH)_2^0$ and adsorption of $(OH)^+$. The adsorption property of amine-functionalized corn husk-derived activated carbon (CHAC.NH₂) was observed to be based on the presence of NH₂ groups. Therefore the adsorption process can be considered as the competitive adsorption between the dissolved species (Pb²⁺, Cu²⁺, Ni²⁺ and H₃O⁺ and -NH₂ groups). At lower pH the number of H₃O⁺ plays a leading role than that of others and the surface of the adsorbent is most likely covered with H₃O⁺ ions. The protonized amino groups then passivate the adsorption sites and hence decrease the adsorption of other metal ions. Under alkaline pH condition, the -NH₂ on the CHAC.NH₂ surface are deprotonated and the surface of the adsorbent becomes negatively charged which favors the removal of metal ions (Pb, Cu and Ni). Nonetheless, at much higher pH (> 8), precipitation was noticed and thus attributed to metal hydroxides which further reduce the adsorption of the metals. This can be further illustrated below (Fu *et al.*, 2016).

 $-NH_2 + H_3O^+ \longrightarrow -HN_3^+ + H_2O \qquad (acidic medium)$

 $-NH_2 + OH^- \longrightarrow -NH^- + H_2O$ (alkaline medium)

In general terms, Pb, Cu and Ni ions exist as cations in acidic medium, the surface of the adsorbent in acidic medium is considered to be surrounded by H^+ ions which could compete with the heavy metal ions for adsorption sites, thereby preventing them from approaching the binding sites on the adsorbent. This trend can also be attributed to the electrostatic repulsion or attraction in the adsorption process (Nazari *et al.*, 2016). This protonation decreases the molecular recognition of the adsorbent sites for the metals. The adsorption process started to sharply decrease as pH exceeds 8 which could be attributed their presence as cation molecules in an alkaline environment, thus increasing affinity between excess OH^- ions and the heavy metals ions and resulting in the electrostatic repulsion between adsorbent and the adsorbate as shown in Figure 4.8. The optimum pH zone that neither causes protonation of nitrogen atom onto the amino

groups nor precipitates of metal hydroxides for all the heavy metals (Pb, Cu and Ni) was established at pH range 6-8 (near neutral). This is similar to the findings of Peng *et al.*, 2017 who used amine-functionalized magnetic bamboo-based activated carbon for the removal of pollutants from pharmaceutical wastewater.



Figure 4.8: Effect of solution pH on the adsorptive removal of Pb, Cu, and Ni

4.4 Adsorption Isotherm Models

Adsorption isotherms of Pb, Cu and Ni were obtained from the equilibrium sorption experiment investigated at adsorbent dosage ranging from 0.5 to 5 g. The experimental data were fitted using linearized regression co-efficient according to the Langmuir, Freundlich, Harkin-Jura, Elovich, Dubinin, Temkin, Jovanovic and D-R isotherm models as presented in Table 4.6. The fitted linear plot in Appendices suggests that adsorption rate increased with an increase in dosage. The fitness of the experimental data was determined with the regression correlation coefficient. It was found that the Freundlich model is the most suited model compared to other isotherms. The fitted parameters in Table 4.6 show that highest correlation coefficients were ascribed by Freundlich model. The maximum adsorption capacities of Pb, Cu and Ni using F-CHAC as presented in Table 4.6 were compared with the adsorption capacities of previously prepared adsorbents in Table 4.7 and it reveals less significance when compared to the earlier reported modified biomass based activated carbons. This could be attributed to the presence of other co-existing heavy metals and organic impurities (Cr, Zn, Fe, BOD, COD and TOC) at extreme concentrations whose adsorption may have been more favored by the process over heavy metals of interest (Pb, Cu and Ni). (Kamaruzaman et al., 2020). The Freundlich model explains the heterogeneous active sites present in the adsorbent and the results are in agreement with the finding of Xu et al. (2020). The adsorption intensity (1/n) values in Freundlich model for the pollutants lies between 0 > (1/n) < 1 indicating identical adsorption process and adsorption energy for all sites, it also suggests that the adsorbent is good for removal of the heavy metals. In addition it is also stated that the use of these isotherms could tacitly change the error variance and normality assumption of standard least squares (Almasian et al., 2017). For authenticity of the fitness of isotherm models, the fitness of equation to the experimental data error function was evaluated. The Chi-square (χ^2) and sum of square error (SSE) tests were used to buttress the best isotherm model as presented in Table 4.6 the lower the error function, the better the isotherm model used for the adsorption of pollutant on to the adsorbent. From Table 4.6, the Freundlich isotherm has the least error function values, showing that the adsorption of the metals from local battery recycling wastewater favorably follows Freundlich model. Overall observation on the eight isotherm models employed in terms of correlation coefficient and error analysis revealed that this study follows the trend Freundlcih > Temkin > Jovanovic > Dubinin> Elovich >Langmuir> Harkin-Jura> D-R

Isotherm	Parameter	Pb	Cu	Ni
Langmuir	Qm	2.8137	0.7236	0.3369
	Q _e	2.2580	1.4920	1.0650
	K _L	0.5392	0.1526	0.1104
	R ²	0.9056	0.9716	0.8490
	SSE	0.31	0.59	0.53
	χ^2	0.11	0.82	1.57
Freundlich	K _F	1.7968	1.0321	0.6978
	Q _e	2.2580	1.4920	1.0650
	1/N	0.3139	0.3745	0.5287
	R ²	0.9743	0.9316	0.9266
	SSE	0.21	0.21	0.14
	χ^2	0.12	0.20	0.20
Harkin-Jura	В	1.6874	1.6806	1.6623
	А	5.988	2.7655	1.1429
	Qe	2.2580	1.4920	1.0650
	\mathbb{R}^2	0.8058	0.7109	0.9135
	SSE	13.91	1.62	0.06
	χ^2	2.32	0.59	0.05
Elovich	Ke	2.3535	1.2054	1.2399
	Q_{m}	1.6984	1.5929	2.9069
	Qe	2.2580	1.4920	1.0650
	\mathbb{R}^2	0.9466	0.9221	0.6252
	SSE	0.313	0.010	3.393
	χ^2	0.180	0.006	1.167

	Table 4.6: Adsorption isotherm	parameters for Pb, Cu and Ni
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Isotherm	Parameter	Pb	Cu	Ni
D-R	K _{D-R}	3.0×10 ⁻⁷	1.0×10 ⁻⁶	3.0×10 ⁻⁶
	Е	-1290	-707	-408
	Qe	2.2580	1.4920	1.0650
	q_{m}	4.4777	3.4573	2.2922
	R ²	0.7087	0.8849	0.5754
	SSE	4.937	3.862	1.506
	χ^2	1.103	1.117	0.657
Dubinin	В	73.70	39.60	49.70
	Qe	6.74	4.65	3.63
	Q_{m}	11.77	10.87	10.91
	\mathbb{R}^2	0.9571	0.9606	0.9443
	SSE	25.30	38.69	52.99
	χ^2	2.149	3.559	4.857
Temkin	В	7.134	5.635	4.077
	K _T	3.5639	3.2749	2.9383
	Qe	6.438	4.835	4.397
	\mathbb{R}^2	0.9719	0.9656	0.9339
	SSE	8.26	2.43	2.13
	χ^2	2.318	0.742	0.725
Jovanovic	KJ	106.98	76.80	62.76
	Q _{max}	5.415	4.953	4.653
	Qe	2.073	1.789	1.568
	R ²	0.9898	0.9857	0.9827
	SSE	11.169	10.011	9.517
	χ^2	2.063	2.021	2.045

 Table 4.6: Adsorption isotherm parameters for Pb, Cu and Ni contd.

Adsorbent	Adsorption capacity (mg/g)	Metal ion	Experimental condition	Reference
Cobalt ferrite- supported activated carbon	6.27 23.6	lead and chromium ions from tannery wastewater	pH:5, contact time:80 min, dosage:0.8 g and temperature: 333K	Yahya <i>et al.,</i> 2020d
Functionalized Magnetic Nanoparticles on Activated Carbon	80 % 53 %	Pb(II) and Cr(VI) Ion	Contact time 3 h, pH 2, Temperature 25 °C	Fatehi <i>et al.</i> , 2017
magnetic activated carbon incorporated with amino groups	104.20	Pb(II)	Dosage 1.0 g/L, pH 2	Fu <i>et al.,</i> 2016
EDTA modified yeast biomass coated with magnetic chitosan micro particle	134.90	Pb(II)	Contact time 120 min, Temperature 30 °C	Li <i>et al.</i> , 2013
Magnetic iron oxide (Fe3O4) nanoparticles from tea waste	4.81	Arsenic	Contact time 30 min, pH 6, Dosage 3 g/L, Temperature 30 °C	Lunge <i>et al.</i> , 2014
Magnetic Activated Carbon Derived from biomass (Coconut shell) Waste	3.23	Toxic dyes	Contact time 2 h, Dosage 2 g/L, pH 6.1, Temperature 25 °C	Cazetta <i>et al.,</i> 2016
Functionalized	7.95	Pb	Contact time 60	This work
Activated carbon	6.08	Cu	min, Dosage 1 g, Temperature 30 °C,	
	4.99	Ni	pH 2	

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4.5 Adsorption Kinetic Models

The adsorption data on the removal of heavy metals from local battery recycling wastewater was subjected to kinetic analysis and the results presented in Table 4.8, from the Tables, the kinetic models parameters were fitted by Pseudo-first-order, Pseudo-second-order, Elovich and Intra-particle diffusion kinetic models. The correlation coefficient of the Pseudo-second-order model described the data better, suggesting that the reaction depends on the contact time and the concentrations of the heavy metals in the wastewater. This suggests that Chemisorption played a significant role in the adsorption process (Xu *et al.*, 2020). Noticeability, the calculated k_2 value was highest for Pb(II) ions followed by Ni(II) and Cu(II) ions, which was based on the ionic radius mechanism of the adsorbed metal ions on the adsorbents. This conforms to the report of Mustapha *et al.* (2021) who stated that the more the hydrated ionic radius the higher is the rate constant value of the pseudo-second-order.

First-order	k ₁	q _{e theo}	q _{e exp}	R ²	SSE	χ^2
Pb	0.002	5.2735	6.422	0.727	1.32	0.25
Cu	0.004	3.0063	4.844	0.718	3.38	0.69
Ni	0.007	1.9073	4.393	0.825	6.18	1.41
Second-order	k ₂	q _{e theo}	q _{e exp}	R ²	SSE	χ^2
Second-order Pb	k ₂ 0.0065	q _{e theo}	q _{e exp} 6.422	R² 0.9908	SSE 0.16	χ ² 0.02
Second-order Pb Cu	k ₂ 0.0065 0.0035	q e theo 6.826 5.173	q _{e exp} 6.422 4.844	R² 0.9908 0.9453	SSE 0.16 0.11	χ ² 0.02 0.02

Table 4.8: Adsorption kinetic parameters of Pb, Cu and Ni

Intra-particle diffusion	Ki	q _{e theo}	q _{e exp}	R ²	SSE	χ^2
Pb	0.3197	3.1954	6.422	0.8317	10.41	3.26
Cu	0.2405	2.2159	4.844	0.9195	6.91	3.12
Ni	0.3203	0.8183	4.393	0.9867	12.78	16.89
Elovich	В	q _{e theo}	q _{e exp}	R ²	SSE	χ^2
Elovich Pb	B 0.9639	q _{e theo} 5.0301	q _{e exp} 6.4385	R² 0.9639	SSE 1.9836	χ ² 0.3943
Elovich Pb Cu	B 0.9639 1.3425	q _{e theo} 5.0301 3.6568	q _{e exp} 6.4385 4.8455	R² 0.9639 0.9727	SSE 1.9836 1.4130	χ ² 0.3943 0.3864

Table 4.8: Adsorption kinetic parameters of Pb, Cu and Ni contd.

4.6 Thermodynamic Study

The adsorption studies of Pb, Cu and Ni were examined at 28-65 °C. The values of change in enthalpy, change in entropy and change in free Gibb's energy were determined and presented in Table 4.9. A negative value of ΔH° represents an exothermic adsorption process that shows a release of heat upon adsorption. The negative value of ΔG° denotes that the adsorption of the heavy metals by F-CHAC is a spontaneous and feasible process. The positive value of entropy (ΔS°) shows that the adsorption of metals has greater stability without any structural alteration in the solid-liquid interface. Cui *et al.* (2020) noticed similar observations on the adsorption of phenol and para-nitrophenol onto corn husk derived magnetized activated carbon. They found that ΔG° at all temperatures for the adsorption of metals were negative and spontaneous.

Heav y	∆H (kJ ∕mol	$\Delta S(\frac{J}{mol})$	R ²	•			ΔG	(kJ/m	ol)			
metal s		/К		301 K	303 K	308 K	313 K	318 K	323 K	328 K	333 K	338 K
Ph	-11 /7	23.92	0.965	_	-	_	_	_	-	_	_	_
10	-11.47	23.72	1	4.47	4.52	4.18	3.55	3.49	3.55	3.60	3.65	3.75
Cu	-9.70	14.29	0.931	-	-	-	-	-	-	-	-	-
			1	5.55	5.63	5.42	4.79	4.85	4.92	4.98	5.06	5.17
Ni	-5.97	3.54	0.997	-	-	-	-	-	-	-	-	-
			0	4.97	5.04	4.93	4.63	4.70	4.73	4.78	4.85	4.93

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4.7 **Regeneration Study**

The regeneration experiment for F-CHAC was investigated and the adsorption capacity of the adsorbent after each cycle is presented in Table 4.10. The result shows that the F-CHAC has high adsorption capacities for Pb, Cu and Ni ions after the first 3 repeated cycles with near 100 % adsorbent regeneration, this however reduces gradually after the third run as the desorption efficiency drops from 33 to 25%. This is also depicted by Figure 4.9 where the removal efficiency for each cycle is presented. This further suggests collapse of the inner and outer pores or gradual blockage of the active sites that leads to change in structural composition of the adsorbent due to extensive exposure to HCl over time of desorption recycle. The adsorbent regeneration becomes less feasible as desorption continue due to the change in structural efficiency of the adsorbent as a result of prolong usage. Similar trend was reported by Gautam et al., 2014 while studying the use of biomass-derived adsorbent for the removal of Pb, Cd and Ni metal ions from aqueous solution.

Tuble 11/1 Description and recovery enterency of r entries							
No. of	Amount dese	orbed		%	%Re		
recycles				Desorption			
	Pb (mg/g)	Cu (mg/g)	Ni (mg/g)	_			
1	6.1995	4.1515	3.3485	33.32	100		
2	C 1505	4 1505	2 2155	22.15	00.22		
2	0.1385	4.1505	3.3155	33.15	99.33		
3	6.1545	4.147	3.3005	32.97	99.27		
4	5.371	3.634	3.1595	28.00	86.63		
5	4 349	3 199	2,899	25.25	70.15		
2	1.5 17	5.177	2.077	20.20	10.10		

Table 4.9: Desorption and recovery efficiency of F-CHAC



Figure 4.10: Removal efficiency of F-CHAC after 5 cycles

CHAPTER FIVE

5.0 CONCLISIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of heavy metal removal from local battery recycling wastewater using functionalized corn husk derived activated carbon was achieved with good efficiency. The presence of various constituent like the fixed carbon and VOCs in high percentages as obtained from the proximate analysis establishes the suitability of corn husk as activated carbon precursor. The introduction of nitrogen containing groups into the framework of the activated carbon confirms the amine functionalization of the corn husk derived adsorbent

The presence of numerous pores with very high surface area as obtained from the SEM and BET analysis confirms the availability of sorption sites on F-CHAC for heavy metal removal. The optimum contact time of 95, 125 and 125 min was established for Pb and Cu, Ni removal respectively with removal efficiency of 99.36, 97.95 and 95.92 % at an optimal dosage of 3 g. The adsorption efficiency as influenced by temperature (optimum 45 ^oC) and pH (Pb:4, Cu:5 and Ni:6) shows exothermic sorption process as increased removal efficiency was achieved at certain high temperature and pH while further increase lead to lower sorption

The individual adsorption capacity varies with concentration (10 % effluent concentration: Pb 7.95 mg/L, Cu 6.08 mg/L and Ni 4.99 mg/L. 100 % effluent concentration: Pb 6.32 mg/L Cu 4.15 mg/L and Ni 3.35 mg/L) and the Fruendlich isotherm established the multilayer adsorption process with best fit in experimental adsorption capacity as compared to other isotherms. The second order kinetic model

93

was the best fit for the adsorption kinetics which confirms chemisorption played the most significant role in the sorption study.

The values of enthalpy and Gibb's free energy further establish the exothermic and spontaneous nature of the adsorption process. The high removal efficiency of the adsorbent after three cycles confirms the regeneration and reuse of the adsorbent for heavy metal removal.

5.2 Recommendations

The following recommendations are necessary for further research studies.

- The study of the removal of other non-metal pollutants like the BOD, COD, TOC and TSS should be investigated
- 2. Optimization of the process parameter using design expert to obtain optimum process parameters for column study should be investigated.
- 3. The use of other biomass based functionalized activated carbon in the removal of heavy metals from local battery recycling wastewater should be further studied

5.3 Contribution to Knowledge

- 1. The synthesis of an amine functionalized activated carbon from corn husk was achieved with a significant improvement in the surface area from 92.1 m²/g to $442.70 \text{ m}^2/\text{g}$
- Analysis of the collected effluent wastewater from local battery recycling processes reveals the presence of several non-degradable toxic pollutants (Pb, Cu, Ni, Zn, Cr and Fe) in extreme concentrations

- 3. An optimum contact time of 95, 125 and 125 min was established for Pb, Cu and Ni ions removal respectively with a corresponding removal efficiency of 99.36
 %, 97.95 % and 95.92 % at an optimum dosage of 3 g.
- 4. A high removal efficiency of 99 % for Pb, Cu and Ni was achieved after three adsorption cycles which confirms the reusability of the adsorbent for heavy metal removal from local battery recycling wastewater.

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APPENDICES

Effect of effluent concentration

%	Pb ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)
concentration			
(mg/L)			
10	94.8125	99.68085	99.84
20	89.71875	98.75614	98.31
30	82	97.52046	97.96
40	82.70313	95.08183	94.61
50	79.7125	92.81506	92.44
60	77.57292	89.9509	90.67
70	76.58036	83.65794	85.88
80	79.15625	74.40262	78.81
90	79.06944	71.21931	70.29
100	79	68.05237	66.99

Effect of contact time

Time	Pb ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)
(min)			
5	38.2875	37.92962	28.74
20	60.6875	60.45827	43.51
35	68.1	62.00491	56.98
50	73.4375	64.0671	64.26
65	77.48125	68.06874	67.19
80	79.3875	72.76596	73.09
95	80.275	75.45827	80.06
110	80.35	78.04419	86.15
125	80.45	79.27987	87.86
140	80.48125	79.30442	87.94

Effect of adsorbent dosage

Dosage	Pb ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)	
(g)				
0.5	41.7	36.00655	38.2	
1	77.49375	68.10966	66.97	
1.5	86.73125	85.60556	78.62	
2	94.95625	92.99509	85.91	
2.5	99.7625	98.37152	94.84	
3	99.93125	99.78723	98.18	
3.5	99.99375	99.93453	99.87	
4	99.99375	99.99182	99.93	
4.5	99.99375	99.99182	99.99	
5	99.99375	99.99182	99.99	

Effect of effluent pH

рН	Pb ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)
2	77.45	68.06056	67
3	80.575	73.66612	70.15
4	81.11875	77.06219	74.68
5	81.24375	78.56792	76.78
6	81.31875	78.70704	78.77
7	81.31875	78.70704	78.79
8	81.24375	78.64157	78.78
9	79.925	77.43044	75.35
10	78.7375	73.10966	72.09
11	77.43125	72.40589	70.69

Effect of effluent temperature

Temperature	Pb ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)
(°C)			
25	76.7	68.01964	66.88
30	76.81875	68.07692	67.01
35	79.56875	70.65466	68.79
40	83.60625	76.00655	72.65
45	84.19375	76.14566	73.11
50	80.63125	76.09656	71.77
55	80.23125	73.10147	66.74
60	80.0125	72.01309	66.21
65	79.86875	65.37643	65.76

fruendlich isotherm

Pb	160				
M (g)	Ce	q (mg)	Q (mg/g)	LogQe	LogCe
	(mg/L)				
0.5	93.28	3.336	6.672	0.824256038	1.969788537
1	36.01	6.1995	6.1995	0.792356664	1.556423121
1.5	21.23	6.9385	4.625667	0.665174334	1.326949994
2	8.07	7.5965	3.79825	0.579583547	0.906873535
2.5	5.83	7.7085	3.0834	0.489029868	0.765668555
3	3.65	7.8175	2.605833	0.415946635	0.562292864
3.5	1.94	7.903	2.258	0.353723938	0.28780173
4	1.03	7.9485	1.987125	0.298225187	0.012837225
4.5	1.01	7.9495	1.766556	0.2471273	0.004321374
5	1.01	7.9495	1.5899	0.201369809	0.004321374



Cu	122.2				
M (g)	Ce	q (mg)	Q (mg/g)	LogQe	LogCe
	(mg/L)				
0.5	78.2	2.19	4.38	0.641474111	1.893206753
1	38.97	4.1515	4.1515	0.618205042	1.590730406
1.5	17.59	5.2205	3.480333	0.541620841	1.245265839
2	10.04	5.598	2.799	0.447002898	1.001733713
2.5	6.85	5.7575	2.303	0.362293938	0.835690571
3	4.82	5.859	1.953	0.290702243	0.683047038
3.5	3.06	5.947	1.699143	0.230229894	0.485721426
4	2.87	5.9565	1.489125	0.172931155	0.457881897
4.5	2.52	5.974	1.327556	0.123052704	0.401400541
5	2.5	5.975	1.195	0.077367905	0.397940009



Ni	100				
M (g)	Ce	q (mg)	Q (mg/g)	LogQe	LogCe
	(mg/L)				
0.5	61.8	1.91	3.82	0.582063363	1.790988475
1	33.03	3.3485	3.3485	0.524850303	1.518908574
1.5	21.38	3.931	2.620667	0.418411785	1.330007701
2	18.65	4.0675	2.03375	0.308297566	1.270678836
2.5	16.93	4.1535	1.6614	0.220474206	1.228656958
3	13.04	4.348	1.449333	0.161168281	1.115277591
3.5	9.87	4.5065	1.287571	0.109771331	0.994317153
4	6.31	4.6845	1.171125	0.068603252	0.800029359
4.5	4.09	4.7955	1.065667	0.027621382	0.611723308
5	4.08	4.796	0.9592	-0.01809083	0.610660163



Langmuir Isotherms

Pb	160				
M (g)	Ce	q (mg)	Q (mg/g)	1/qe	1/Ce
	(mg/L)				
0.5	93.28	3.336	6.672	0.149880096	0.010720412
1	36.01	6.1995	6.1995	0.161303331	0.027770064
1.5	21.23	6.9385	4.625667	0.216185054	0.047103156
2	8.07	7.5965	3.79825	0.263279142	0.123915737
2.5	5.83	7.7085	3.0834	0.324317312	0.171526587
3	3.65	7.8175	2.605833	0.383754397	0.273972603
3.5	1.94	7.903	2.258	0.442869796	0.515463918
4	1.03	7.9485	1.987125	0.503239605	0.970873786
4.5	1.01	7.9495	1.766556	0.566073338	0.99009901
5	1.01	7.9495	1.5899	0.628970375	0.99009901


Cu	122.2				
M (g)	Ce	q (mg)	Q (mg/g)	1/qe	1/Ce
	(mg/L)				
0.5	78.2	2.2	4.4	0.012787724	0.227272727
1	38.97	4.1615	4.1615	0.025660765	0.240297969
1.5	17.59	5.2305	3.487	0.056850483	0.286779467
2	10.04	5.608	2.804	0.099601594	0.356633381
2.5	6.85	5.7675	2.307	0.145985401	0.433463372
3	4.82	5.869	1.956333	0.20746888	0.511160334
3.5	3.06	5.957	1.702	0.326797386	0.587544066
4	2.87	5.9665	1.491625	0.348432056	0.670409788
4.5	2.52	5.984	1.329778	0.396825397	0.752005348
5	2.5	5.985	1.197	0.4	0.835421888



Ni	100				
M (g)	Ce	q (mg)	Q (mg/g)	1/qe	1/Ce
	(mg/L)				
0.5	61.8	1.91	3.82	0.01618123	0.261780105
1	33.03	3.3485	3.3485	0.030275507	0.298641183
1.5	21.38	3.931	2.620667	0.046772685	0.381582295
2	18.65	4.0675	2.03375	0.053619303	0.49170252
2.5	16.93	4.1535	1.6614	0.059066745	0.60190201
3	13.04	4.348	1.449333	0.076687117	0.689972401
3.5	9.87	4.5065	1.287571	0.101317123	0.776655941
4	6.31	4.6845	1.171125	0.158478605	0.853879816
4.5	4.09	4.7955	1.065667	0.244498778	0.938379731
5	4.08	4.796	0.9592	0.245098039	1.042535446



Cu	160					
M (g)	Ce	q (mg)	Q (mg/g)	E	E2	InQ
	(mg/L)					
0.5	93.28	3.336	6.672	26.86250661	721.5942616	1.897919665
1	36.01	6.1995	6.1995	69.00299934	4761.413918	1.824468644
1.5	21.23	6.9385	4.625667	115.9496881	13444.33018	1.531620505
2	8.07	7.5965	3.79825	294.2830997	86602.54279	1.334540434
2.5	5.83	7.7085	3.0834	398.7995085	159041.048	1.126032884
3	3.65	7.8175	2.605833	609.9851749	372081.9136	0.957752522
3.5	1.94	7.903	2.258	1047.261764	1096757.202	0.814479466
4	1.03	7.9485	1.987125	1709.179884	2921295.874	0.68668887
4.5	1.01	7.9495	1.766556	1733.634204	3005487.552	0.569031637
5	1.01	7.9495	1.5899	1733.634204	3005487.552	0.463671121

D-R isotherm



Cu	122.2					
M (g)	Ce	q (mg)	Q (mg/g)	E	E2	InQ
	(mg/L)					
0.5	78.2	2.19	4.38	32.00985889	1024.631066	1.477048724
1	38.97	4.1515	4.1515	63.82763531	4073.967029	1.423469715
1.5	17.59	5.2205	3.480333	139.2915307	19402.13053	1.247128075
2	10.04	5.598	2.799	239.1873097	57210.56911	1.029262211
2.5	6.85	5.7575	2.303	343.2705811	117834.6919	0.834212621
3	4.82	5.859	1.953	474.9246053	225553.3807	0.669366652
3.5	3.06	5.947	1.699143	712.3328903	507418.1466	0.530123922
4	2.87	5.9565	1.489125	753.0785501	567127.3026	0.398188699
4.5	2.52	5.974	1.327556	841.9025166	708799.8474	0.283339323
5	2.5	5.975	1.195	847.6213431	718461.9413	0.178146185



Ni	100					
M (g)	Ce	q (mg)	Q (mg/g)	E	E2	InQ
	(mg/L)					
0.5	61.8	1.91	3.82	40.43653434	1635.113309	1.340250423
1	33.03	3.3485	3.3485	75.13655684	5645.502173	1.208512484
1.5	21.38	3.931	2.620667	115.1545084	13260.56081	0.963428738
2	18.65	4.0675	2.03375	131.57779	17312.71483	0.70988138
2.5	16.93	4.1535	1.6614	144.5687515	20900.12392	0.50766062
3	13.04	4.348	1.449333	186.1364855	34646.79122	0.371103681
3.5	9.87	4.5065	1.287571	243.1144533	59104.6374	0.252757831
4	6.31	4.6845	1.171125	370.5849266	137333.1879	0.157964825
4.5	4.09	4.7955	1.065667	551.0191357	303622.0879	0.063600581
5	4.08	4.796	0.9592	552.2318826	304960.0521	-0.04165567



Elovich Isotherm

Pb	160					
M (g)	Ce	q (mg)	Q (mg/g)	qe/Ce	lnqe/ce	qe
	(mg/L)					
0.5	93.28	3.336	6.672	0.071527	-2.63769	6.672
1	36.01	6.1995	6.1995	0.172161	-1.75933	6.1995
1.5	21.23	6.9385	4.625667	0.217883	-1.52379	4.625667
2	8.07	7.5965	3.79825	0.470663	-0.75361	3.79825
2.5	5.83	7.7085	3.0834	0.528885	-0.63698	3.0834
3	3.65	7.8175	2.605833	0.713927	-0.33697	2.605833
3.5	1.94	7.903	2.258	1.163918	0.151791	2.258
4	1.03	7.9485	1.987125	1.929248	0.65713	1.987125
4.5	1.01	7.9495	1.766556	1.749065	0.559081	1.766556
5	1.01	7.9495	1.5899	1.574158	0.453721	1.5899

Cu	122.2				
M (g)	Ce (mg/L)	q (mg)	Q (mg/g)	qe/Ce	lnqe/ce
0.5	78.2	2.2	4.4	0.056266	-2.87767
1	38.97	4.1615	4.1615	0.106787	-2.23692
1.5	17.59	5.2305	3.487	0.198238	-1.61829
2	10.04	5.608	2.804	0.279283	-1.27553
2.5	6.85	5.7675	2.307	0.336788	-1.0883
3	4.82	5.869	1.956333	0.405878	-0.9017
3.5	3.06	5.957	1.702	0.556209	-0.58661
4	2.87	5.9665	1.491625	0.51973	-0.65445
4.5	2.52	5.984	1.329778	0.52769	-0.63925
5	2.5	5.985	1.197	0.4788	-0.73647
Ni	100				
Ni M (g)	100 Ce	M (g)	Ce	M (g)	Ce
Ni M (g)	100 Ce (mg/L)	M (g)	Ce (mg/L)	M (g)	Ce (mg/L)
Ni M (g) 0.5	100 Ce (mg/L) 61.8	M (g) 0.5	Ce (mg/L) 61.8	M (g)	Ce (mg/L) 61.8
Ni M (g) 0.5 1	100 Ce (mg/L) 61.8 33.03	M (g) 0.5 1	Ce (mg/L) 61.8 33.03	M (g) 0.5 1	Ce (mg/L) 61.8 33.03
Ni M (g) 0.5 1 1.5	100 Ce (mg/L) 61.8 33.03 21.38	M (g) 0.5 1 1.5	Ce (mg/L) 61.8 33.03 21.38	M (g) 0.5 1 1.5	Ce (mg/L) 61.8 33.03 21.38
Ni M (g) 0.5 1 1.5 2	100 Ce (mg/L) 61.8 33.03 21.38 18.65	M (g) 0.5 1 1.5 2	Ce (mg/L) 61.8 33.03 21.38 18.65	M (g) 0.5 1 1.5 2	Ce (mg/L) 61.8 33.03 21.38 18.65
Ni M (g) 0.5 1 1.5 2 2.5	100 Ce (mg/L) 61.8 33.03 21.38 18.65 16.93	M (g) 0.5 1 1.5 2 2.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93	M (g) 0.5 1 1.5 2 2.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93
Ni M (g) 0.5 1 1.5 2 2.5 3	100 Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04	M (g) 0.5 1 1.5 2 2.5 3	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04	M (g) 0.5 1 1.5 2 2.5 3	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04
Ni M (g) 0.5 1 1.5 2 2.5 3 3.5	100 Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87	M (g) 0.5 1 1.5 2 2.5 3 3.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87	M (g) 0.5 1 1.5 2 2.5 3 3.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87
Ni M (g) 0.5 1 1.5 2 2.5 3 3.5 4	100 Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31	M (g) 0.5 1 1.5 2 2.5 3 3.5 4	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31	M (g) 0.5 1 1.5 2 2.5 3 3.5 4	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31
Ni M (g) 0.5 1 1.5 2 2.5 3 3.5 4 4.5	100 Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31 4.09	M (g) 0.5 1 1.5 2 2.5 3 3.5 4 4.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31 4.09	M (g) 0.5 1 1.5 2 2.5 3 3.5 4 4.5	Ce (mg/L) 61.8 33.03 21.38 18.65 16.93 13.04 9.87 6.31 4.09



Harkin-Jura Isaotherm

Pb	160					
M (g)	Ce	q (mg)	Q (mg/g)	Qe2	1/Qe2	log Ce
	(mg/L)					
0.5	93.28	3.336	6.672	44.51558	0.022464	1.969789
1	36.01	6.1995	6.1995	38.4338	0.026019	1.556423
1.5	21.23	6.9385	4.625667	21.39679	0.046736	1.32695
2	8.07	7.5965	3.79825	14.4267	0.069316	0.906874
2.5	5.83	7.7085	3.0834	9.507356	0.105182	0.765669
3	3.65	7.8175	2.605833	6.790367	0.147267	0.562293
3.5	1.94	7.903	2.258	5.098564	0.196134	0.287802
4	1.03	7.9485	1.987125	3.948666	0.25325	0.012837
4.5	1.01	7.9495	1.766556	3.120719	0.320439	0.004321
5	1.01	7.9495	1.5899	2.527782	0.395604	0.004321

Cu	122.2					
M (g)	Ce	q (mg)	Q (mg/g)	Qe2	1/Qe2	log Ce
	(mg/L)					
0.5	78.2	2.2	4.4	19.36	0.051653	1.893207
1	38.97	4.1615	4.1615	17.31808	0.057743	1.59073
1.5	17.59	5.2305	3.487	12.15917	0.082242	1.245266
2	10.04	5.608	2.804	7.862416	0.127187	1.001734
2.5	6.85	5.7675	2.307	5.322249	0.18789	0.835691
3	4.82	5.869	1.956333	3.82724	0.261285	0.683047
3.5	3.06	5.957	1.702	2.896804	0.345208	0.485721
4	2.87	5.9665	1.491625	2.224945	0.449449	0.457882
4.5	2.52	5.984	1.329778	1.768309	0.565512	0.401401
5	2.5	5.985	1.197	1.432809	0.69793	0.39794

Ni	100					
M (g)	Ce	q (mg)	Q (mg/g)	Qe2	1/Qe2	log Ce
	(mg/L)					
0.5	61.8	1.91	3.82	14.5924	0.068529	1.790988
1	33.03	3.3485	3.3485	11.21245	0.089187	1.518909
1.5	21.38	3.931	2.620667	6.867894	0.145605	1.330008
2	18.65	4.0675	2.03375	4.136139	0.241771	1.270679
2.5	16.93	4.1535	1.6614	2.76025	0.362286	1.228657
3	13.04	4.348	1.449333	2.100567	0.476062	1.115278
3.5	9.87	4.5065	1.287571	1.65784	0.603194	0.994317
4	6.31	4.6845	1.171125	1.371534	0.729111	0.800029
4.5	4.09	4.7955	1.065667	1.135645	0.880557	0.611723
5	4.08	4.796	0.9592	0.920065	1.08688	0.61066



Pseudo-First order Kinetic Model

T (min)	Pb	Cu	Ni
	LnCt	LnCt	LnCt
5	1.119395	0.840489018	0.362557607
20	1.580009	1.306709882	0.777258523
35	1.695249	1.331970162	1.046968056
50	1.770706	1.364687607	1.16720508
65	1.824307	1.425274661	1.211792153
80	1.848612	1.492004816	1.295959285
95	1.85973	1.528336311	1.38704408
110	1.860663	1.56203179	1.460357689
125	1.861907	1.577740826	1.480012365
140	1.862296	1.578050439	1.48092249



T (min)	Pb	Cu	Ni
	t/qt	t/qt	t/qt
5	1.632387	2.157497303	3.47947112
20	4.119464	5.414185165	9.193288899
35	6.424376	9.238484888	12.28501229
50	8.510638	12.77302337	15.56178027
65	10.48641	15.62875691	19.34811728
80	12.59644	17.9937022	21.89081954
95	14.7929	20.60514044	23.73220085
110	17.11263	23.06805075	25.53685432
125	19.422	25.80511974	28.45435921
140	21.7442	28.89278712	31.83989083

Pseudo-Second order Kinetic Model



Intra-particle Diffusion

t0.5	Pb		Cu		Ni	
	Ce	qt	Ce	Qt	Ce	Qt
	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(mg/g)
2.2361	98.74	3.063	75.85	2.3175	71.26	1.437
4.4721	62.9	4.855	48.32	3.694	56.49	2.1755
5.9161	51.04	5.448	46.43	3.7885	43.02	2.849
7.0711	42.5	5.875	43.91	3.9145	35.74	3.213
8.0623	36.03	6.1985	39.02	4.159	32.81	3.3595
8.9443	32.98	6.351	33.28	4.446	26.91	3.6545
9.7468	31.56	6.422	29.99	4.6105	19.94	4.003
10.4881	31.44	6.428	26.83	4.7685	13.85	4.3075
11.1803	31.28	6.436	25.32	4.844	12.14	4.393
11.8322	31.23	6.4385	25.29	4.8455	12.06	4.397



Thermodynamics

	Pb		Cu		Ni	
1/T	LnKc	ΔG°	LnKc	ΔG°	LnKc	ΔG°
0.003356	-	-	-	-	-	-
	1.804283926	4470.243334	2.241057754	5552.381942	2.006334761	4970.838826
0.0033	-	-	-	-	-	-
	1.797627285	4528.478394	2.238423149	5638.905768	2.000943618	5040.661107
0.003247	-	-	-	-	-	-
	1.636176437	4189.776637	2.117061752	5421.185432	1.925721219	4931.217435
0.003195	-1.36651416	-	-	-	-	-4637.40508
		3556.055202	1.842693813	4795.208942	1.782053244	
0.003145	-	-3497.86118	-	-4851.60115	-	-
	1.323017015		1.835050203		1.779270648	4704.128262
0.003096	-	-	-	-	-1.7620175	-
	1.322547292	3551.597595	1.832796263	4921.831407		4731.760559
0.003049	-	-	-	-	-	-
	1.321607395	3604.012793	1.828280382	4985.705975	1.755916675	4788.370725
0.003003	-	-	-	-	-	-
	1.319725785	3653.742658	1.828732452	5062.959174	1.754505878	4857.458302
0.002959	-	-	-	-	-	-
	1.321137219	3712.569977	1.841796144	5175.690281	1.754505878	4930.393111



Desorption study

Runs	M _f (g)	Pb		Cu		Ni	
		Ce	%	Ce mg/L	% removal	Ce mg/L	% removal
		mg/L	removal				
1	1.332	36.01	77.49375	38.97	68.05737705	33.03	66.97
2	1.326	36.83	76.98125	38.99	68.04098361	33.69	66.31
3	1.319	36.91	76.93125	39.06	67.98360656	33.99	66.01
4	1.12	52.58	67.1375	49.32	59.57377049	36.81	63.19
5	1.01	73.02	54.3625	58.02	52.44262295	42.02	57.98