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DEPARTMENT OF CHEMISTRY



SYNTHESIS AND CHARACTERIZATION OF LOW COST ACTIVATED CARBON PREPARED FROM WATER HYACINTH STEM BY PHOSPHERIC FOR REMOVAL OF CHROMIUM ION IN AQUEOUS SOLUTION, EQUILIBRIUM AND KINETIC STUDY

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Synthesis and Characterization of Low Cost Activated Carbon Prepared from Water Hyacinth Stem by Phosphoric Acid for Removal of Chromium Ion in Aqueous Solution, Equilibrium and Kinetic Study

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APPROVAL SHEET I

This is to certify that the thesis entitled “**Synthesis and Characterization of Low Cost Activated Carbon Prepared from Water Hyacinth Stem by Phosphoric Acid for Removal of Chromium Ion in Aqueous Solution, Equilibrium and Kinetic Study**” submitted in partial fulfillment of requirements Degree of Master of Science in Chemistry, College of Natural and Computational Science, Debre Berhan University and is a faithful record of original research work carried out by Dagne Tefera Under my guidance and supervision. No part of this thesis has been submitted for any other degree or diploma. It is further certified that the assistance and help received by him from various sources during the course of investigation has been duly acknowledged. Therefore, I recommend that it be accepted as fulfilling the thesis requirement Submitted by:

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APPROVAL SHEET II

We, the undersigned members of the board of the examiners of the final open defense by Dagne Tefera G/Ki have read and evaluated his thesis entitled “Synthesis and Characterization of Low Cost Activated Carbon Prepared from Water Hyacinth Stem by Phosphoric Acid for Removal of Chromium Ion in Aqueous Solution, Equilibrium and Kinetic Study” and examined the candidates. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

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ACRONYMS AND ABBREVIATIONS

AC	Activated Carbon
BET	Brunauer,Emmet and Teller
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
GAC	Granular Activated Carbon
PAC	Powder Activated Carbon
FT-IR	Fourier Transformation Infrared
AAS	Atomic Absorption Spectroscopy
SWH	Stem of Water Hyancith
E.C	Eichhornia Crassipes

Table of Contents

ACKNOWLEDGEMENT	IV
ACRONYMS AND ABBREVIATIONS	V
LIST OF TABLES	IX
LIST OF FIGURES	X
ABSTRACT	XI
1.INTRODUCTION	1
1.1 Back Ground of The Study	1
1.2 Statement of the Problem	5
1.3. Significance of The Study	6
1.4 Objectives of the Study	7
1.4.1 General Objective.....	7
1.4.2 Specific Objective	7
2.REVIEW LITERATURE	8
2.1 Heavy Metals Source And Toxicity	8
2.2 Chromium	10
2.2.1 Chromium Accumulation And Toxicity	10
2.3 WATER HYACINTH	11
2.4 CHROMIUM REMOVAL TECHNOLOGIES	12
2.4.1 Chemical Precipitation	13
2.4.2 Reduction	13
2.4.3 Ion Exchange.....	14
2.4.4 Solvent Extraction	14
2.4.5 Electrodeposition.....	14
2.4.6 Electrodialysis	15

2.4.7 Adsorption.....	15
2.4.7.1 Physisorption.....	16
2.4.7.2 Chemisorption.....	17
2.5 Mechanism of Adsorption	18
2.6 Adsorbents for Chromium Removal	19
2.6.1 Commercial Activated Carbon.....	19
2.6.2 Non-conventional Low Cost Activated Carbon	20
2.7 Preparation of Activated Carbon	21
2.7.1 Physical Activation	21
2.7.1.1 Carbonization.....	21
2.7.1.2 Activation of Carbonized Intermediate Product with Gaseous Agents.....	22
2.7.2 Chemical Activation.....	22
2.8 Factors Affecting Adsorption of Cr(VI) Ion.....	23
2.8.1 The effect of Initial Chromium Concentration	23
2.8.2 Effect of Solution pH on Adsorption.....	24
2.8.3 Effect of Contact Time.....	24
2.8.4 Effect of Adsorbent Dose	24
2.8.5 Effect of Temperature	25
2.9 Characterization of Activated Carbon	25
2.10 Equilibrium Adsorption Isotherm Models	27
2.10.1 Langmuir Isotherm Model.....	27
2.10.2 Freundlich Isotherm Model	29
2.11 Kinetics Studies.....	30
3. MATERIALS AND METHODS	31
3.1. Chemicals And Instruments	31
3.1.1. Instruments and Equipments	31
3.1.2. Chemicals and Materials	31
3.2 Experimental Methods and Procedures	32
3.2.1 Raw Material Preparation.....	32
3.2.2 Preparation of Activated Carbon	32
3.3 Characterization of the Prepared Activated Carbon	33
3.3.1 FT-IR Spectroscopy	33
3.3.1.1 FTIR of Water Hyacinth Stem Activated Carbon	33
3.3.1.2 FTIR of Metal Loaded Water Hyacinth Stem Activated Carbon.....	34
3.3.2 Preparation of Adsorbent.....	34

3.4 Preparation of Adsorbate Solution (Synthesized Solution)	35
3.4.1 Calibration of Cr(VI) Ion Absorbance	35
3.5 Batch Adsorption Experiments	36
3.5.1 Factors Affecting The Batch Equilibrium Studies	37
3.5.2 Effect of Contact Time	38
3.5.3 Effect of Adsorbent Dosage	38
3.5.4 Effect of pH.....	39
3.5.5 Effect of Initial Concentration.....	39
3.6 Kinetic Models of Heavy Metal Adsorption on Water Hyacinth	39
4. RESULT AND DISCUSSION	41
4.1 Characterization of Prepared Samples	41
4.1.1 The FT-IR Spectroscopy	41
4.1.2 XRD Analysis	42
4.2 Effect of Some Experimental Conditions on Cr(VI) Ions Adsorption from Aqueous Solutions	43
4.2.1 Effect of pH Solution	44
4.2.2 Effect of Adsorption Time	45
4.2.3 Effect of Adsorbent Dosage	46
4.2.4 Effect of Initial Cr(VI) Ions Concentration	47
4.3 Adsorption Isotherms	49
4.3.1 The Langmuir Isotherm.....	49
4.3.2 The Freundlick Isotherm	50
4.4 Adsorption Kinetics	52
5. CONCLUSIONS AND RECOMMENDATIONS	55
5.1 CONCLUSIONS	55
5.2 Recommendation	55
6. REFERENCES	56

LIST OF TABLES

Table	Page
Table 2. 1 Types of Isotherm for Various RL.....	28
Table 2. 2 Freundlich Constant Characteristics (N).....	29
Table 4. 1 FTIR Spectrum of SWH AC before and after Adsorption	42
Table 4. 2 Comparison of Adsorption % Cr (Vi) Ion onto Water Hyacinth and other Different Adsorbents Found in Literatures.	48
Table 4. 3 Parameters for Langmuir and Freundlich Isotherms for Adsorption of Chromium Ions on SWH Activated Carbon	51

LIST OF FIGURES

Figure 3. 1 Pretreatment of Water Hyacinth.....	32
Figure 3. 2 Water Hyacinth Stem Activation.....	33
Figure 3. 3 Calibration Curve for Cr(Vi) Ion Versus Absorbance	36
Figure 3. 4 (a) Working Solution (b) Optimization	37
Figure 4. 1 (a) SWH AC before Adsorption (b) SWH AC after Adsorption.....	42
Figure 4. 2 XRD Diffractogram of SWH AC	43
Figure 4. 3 ; Effect of pH on Removal Efficiency of Cr(Vi) Ion from Aqueous Solution Using Water Hyacinth Activated Carbon at : $C_0=30$ Ppm , $t= 60$ Minutes and Adsorbate Dose= 1.0 Gram	45
Figure 4. 4: Effect of Contact Time on Removal Efficiency of Cr(Vi) Ion from Aqueous Solution Using Water Hyacinth Activated Carbon at : pH =2 , Adsorbent Dose=1.0 Gram and $C_0 = 30$ Ppm	46
Figure 4. 5 ; Effect of Adsorbent Dose on Removal Efficiency of Cr(Vi) Ion from Aqueous Solution Using Water Hyacinth Activated Carbon at : pH =2 , $t= 60$ Minutes and $C_0 = 30$ Ppm.....	47
Figure 4. 6 ; Effect of Initial Concentration on Removal Efficiency of Cr(Vi) Ion from Aqueous Solution Using Water Hyacinth Activated Carbon at : pH = 2, $t= 60$ Minutes and Adsorbate Dose= 1.0 gram.....	48
Figure 4. 7 Linearized Langmuir Plot for the Adsorption of Cr(Vi) Ion onto SWH AC	50
Figure 4. 8 Linearized Freundlich Plot for the Adsorption of Cr(Vi) Ion onto SWH AC.....	51
Figure 4. 9 Pseudo First Order Kinetics for the Adsorption of Cr(Vi) Ion on SWH AC	53
Figure 4. 10 Pseudo Second Order Kinetics for the Adsorption of Cr(Vi) Ion on SWH AC.....	53

ABSTRACT

Stem of Water Hyacinth (SWH), an aquatic plant in lake Awash was low cost raw material which was used to prepare activated carbon. It was synthesized by chemical activation using phosphoric acid followed by carbonization at 550 °C for 1:30 hours. The activated carbon was used to remove Cr(VI) from aqueous solutions. The concentration of Cr(VI) was determined by UV-visible spectroscopy instrument. For obtaining its maximum removal, batch experiments were carried out at different parameters including initial Cr(VI) ion concentrations, mass of adsorbent, contact time and pH of the solutions were studied. The FT-IR spectra of SWH activated carbon before and uptake of Cr(VI) were recorded to explore the nature of the functional groups responsible for its binding onto the adsorbent. FT-IR band results were obtained at 3424, 2371, 1639, 1169 and 1007 cm⁻¹ (O-H stretch, C-H stretch, C=O stretching, and C=C bending vibrations respectively). The SWH activated carbon XRD result showed the appearance of the one peak at 20° in the XRD result meets some developed crystallinity but fitted with amorphous materials. The maximum removal of Cr(VI) ion (95.5%) was achieved at pH= 2, adsorbent dosage=1.0 gram, time 60 min at Cr(VI) ion concentration 30 mg/L. The equilibrium characteristics of Cr(VI) adsorption was described and the data fitted by Langmuir and Freundlich isotherms equations. But Freundlich isotherm with higher R²(0.995) was best fitted to the experimental values. The R² value for pseudo-first order(0.874) in the adsorption of Cr(VI) ions were higher than that of pseudo-second order(0.226) for the Chromium metal ion. The kinetics data was best fitted with the pseudo-first order type. Adsorbent present in this study was prepared at laboratory scale and its efficient for Cr(VI) ion from aqueous solution and could be an alternative promising weed plant based on adsorbent in field.

Key words: Adsorption, activated carbon, Langmuir-Freundlich isotherm models, water hyacinth, surface composition

1.INTRODUCTION

1.1 Back Ground of The Study

The removal of heavy metal contaminants from aqueous solutions is one of the most important environmental concerns because metals are bio refractory and are toxic to many life forms. Awareness of water pollution has been a major concern for environmentalists globally. The main source of water contamination include, aqueous solution effluent, industrialization (chemical industries, example, petrochemical, metal plating, paper and pulp, food, leather tanning, pharmaceutical, coal, textile, etc.), municipal wastewater, agricultural activities (use of pesticides and herbicides in agriculture, etc) and other environmental and gobal changes (Zhou et al. 2015; Yao et al. 2016a; Trujillo-reyes et al. 2014). Water pollution from heavy metals is a major concern especially in developing countries. The discharge of effluents containing heavy metals into water resource is a serious pollution problem which affects the qaulity of water supply.

The focus of environmental research has largely been centred on municipal or industrial wastewater because of the potential impact to mankind (Mailler et al. 2016). Municipal and industrial wastewater contains many toxic heavy metals such as chromium(Cr), cadmium(Cd), zink(Zn), lead(Pb), copper(Cu), iron(Fe), mercury(Hg), arsenic(As), silver(Ag) and the platinum group elements. Discharging these elements into the environment leads to serious soil and water pollution (Nezamzadeh-ejhieh and Kabiri-samani 2013). Increasing concentration of these metals has a serious threat to humans as they are non-degradable and toxic. They can slowly accumulate in the body of human beings thereby exceeding permissible levels, and causing various diseases such as cancer and nervous system damage (Mailler et al. 2016).

Among the heavy metals, chromium is a heavy metal of great significance whose chemical and toxicological effect on living organisms have been studied in detail and serious implications have been withdrawn. Chromium is one of the chemical risks present in aqueous solution. It is mainly found in aqueous solution with two oxidation states Cr(III) and Cr(VI). The trivalent form is an essential nutrient (Vodyanitskii,Y.N,2016). The Cr(VI) is highly toxic, carcinogenic and mutagenic in nature (Jiao,X, 2015), it is highly mobile in soil, soluble and an aquatic system as well as it is strong oxidant capable of being absorbed by the skin (Kamar et al., 2014). Waste

containing Chromium in the hexavalent form in solution is may result from a different operations like steel manufacture, electroplating, leather tanning, chemical manufacturing, variety of industrial products, such as pigments for the manufacture of paints, inks, rubber, ceramics, corrosion inhibitors and fungicides (Khan et al. 2013). Hence the element has become a significant constituent of swage and soil and is a potentially serious pollutant. The permissible limit of Cr(VI) for potable water is 0.05 mg/L and 0.1 mg/L for discharge to inland surface water.

Human health is highly affected when exposed to Cr(VI) in excess of the permissible limit. Health risks caused by Cr(VI) are the perforation of the nasal septum (Mandina et al., 2013), lung cancer (Bidstup et al., 1983), skin ulceration (McCarron et al.,2000) as well as kidney, liver and gastric damage. More recently, several medical studies have evidenced the capacity of Cr(VI) to produce cancer in workers who manipulate chromates (Raovic,2000). One of the main reasons for this risk occurrence is the discharge of industrial wastes and aqueous solution effluents into the aquatic system. Thus, these wastes must be controlled and limited according to standards defined by international organizations and governmental directives. According to WHO the maximum limit hexavalent chromium is 0.05 mg/L in water destined for domestic consumption (WHO, 2003). Due to the great riskiness of hexavalent chromium several treatments occurred for its removal or reduction of Cr(VI).

At present, different technologies are available for the removal of heavy metals ions from aqueous solution and wastewater using treatment systems such as chemical precipitation, oxidation-reduction, ion-exchange, coagulation and flocculation reverse osmosis, membrane filtration, fixation or concentration and adsorption. However, most of these treatment processes are usually very costly and in some cases they tend to generate secondary waste by-products (Zhou et al. 2015; Tounsadi et al. 2016). Among the above methods, the promising process for the removal metal ions from aqueous solution and wastewater is adsorption, because the technique still remains the most effective, economical and common applicable technology widely used over other techniques in global environmental protection areas (Xunjun 2015). Activated carbon is one the most popular adsorbent for the removal of metal ions from aqueous solutions. It is as an adsorbent which has distinct advantages over the conventional methods which include reusability of biomaterial, low operating , selectivity for specific metal, short and

ease operation time, simplicity in design , no chemical sludge and fast adsorption kinetics used for the of heavy metal ions from aqueous solution (Putro et al. 2017).

More over, adsorption processes can remove heavy metal pollutants from aqueous solutions without generation of hazardous by-products (Zhou et al. 2015). Interesting to note is the fact that activated carbon is widely used for the removal of several pollutants because of its porous structure and surface chemical properties (Luo et al. 2015). Activated carbon is a material that consists of hydrophilic functional groups ,high surface area, tuneable pore structure, low acid/base reactivity and thermo-stability ,thus making it an effective adsorbent for sorption processes and catalytic applications (Chen et al. 2012). It has been reported that the surface oxygen-containing functional groups on activated carbon greatly influenced its adsorption performances since the qualities and quantities of these group affect the adsorption sites,hydrophilicity or hydrophobicity and surface charge distribution on the carbon surface (Scala et al. 2011).

The preparation of activated carbon basically by physical and chemical methods.Physical method involves two stages separately, namely carbonization and activation. Chemical methods involves two stages simultaneously. Furthermore, this procedure set to developed high porosity and high yield by activating at low temperature(Izquierdo, 2011). Activating agents used in the chemical process are normally H_3PO_4 , KOH, NaOH, $ZnCl_2$, NaCl, Na_3PO_4 , $KMnO_4$ for various raw materials to yield activated carbon (Reddy and Konaiah, 2006). However, due to the high production cost, activated carbon tends to be more expensive than other adsorbents and this limits its widespread applications. This limitation has indeed investigated a growing interest in the production of low-cost raw materials (Ghouma et al. 2015;Anisuzzaman et al. 2016;Mailler et al. 2016) that are economically attractive and at the same time show similar or better adsorption performance than commercially available activated carbons. There are different materials of activated carbon used for removal of hexavalent chromium, however there is some need to develop more efficient and locally available cheap adsorbents for the removal of Cr(VI).

The present study is intended to produce low cost activate carbon by chemical activation from water hyacinth stem and using it for the removal of Cr(VI) ion from aqueous solutions. Water hyacinth (*Eichhornia crassipes*) a common free floating aquatic plant tha normally occurs in the

form of dense mats, it is a South American native plant that has attained a very broad global distribution in tropical and semi/tropical countries (Hasan et al., 2007). Water hyacinth has attracted global attention for its uncontrolled behavior and rapid spread which causes a disturbance in navigation, irrigation and power generation. This is more serious than one can expect, since it affects at least three different aspects: environmental, health, and economic. Therefore, production of activated carbon from water hyacinth is an alternative to mitigate the negative effects produced by these mats.

The present research was conducted to utilize water hyacinth stems as efficient alternative adsorbent materials to remove chromium(VI) from aqueous solution using two parameter isotherm models. The influence of operating conditions such as contact time, pH, adsorbent dose and initial concentration was studied. The study covered the kinetic study and equilibrium aspects of the adsorption process followed by determination of reaction orders based on capacity of the adsorbent. The kinetics of adsorption depends on the adsorbate concentration, the physical and chemical characteristics of the adsorbent.

Previous studies revealed that water hyacinth has moisture, volatile matter, fixed carbon and ash content of 9.95, 56.30, 17.40 and 16.35 (wt%), respectively. The analysis and design of an adsorption process requires the adsorption equilibrium investigation which gives the most important piece of information in the understanding of the adsorption process (Barakat et al., 2011). Equilibrium studies that give the capacity of the adsorbents for the adsorbate are described by adsorption isotherm, which is usually the ratio between the quantity adsorbed and the remaining in the solution at equilibrium and at fixed temperature (Jgwe and Abia, 2007). The most commonly used isotherm models include Langmuir and Freundlich (Garba and Das, 2016).

The aim of this research is for this purpose, it is proposed to investigate the synthesis (by using experimental design) and characterization of chemically AC produced from water hyacinth stem and its use as adsorbent of Cr(VI) ion in aqueous solution in batch configuration. If the outcome of this research reveals that the low cost activated of water hyacinth stem is an efficient adsorbent for Cr(VI) ions from aqueous solutions, it would provide a dual advantage of minimizing the large quantity of water hyacinth disposed off as waste and use this cheapest

world worst plant for aqueous solutions treatment to decrease negative impact on the environment.

1.2 Statement of the problem

Anthropogenic activities have caused a great harm to the quality our environment. Environmental pollution is regarded as the top challenge facing mankind in the next 50 years and has attracted much attention from both government agencies and scientific communities (Mohanty, 2012). Despite the tremendous progress in effluents from aqueous solution, industrial, agricultural and domestic origin are often charged with pollutants continue to pose a threatening challenge to life and environmental health. The presence of potentially toxic heavy metals in hale air, in drinking water, food chain and readily absorbed into the human body can cause severe physiological or neurological damage to the human body (Zhenchao J.2015). One of such toxic metal of concern is chromium. Chromo aqueous can be accumulated in human body, causing erythrocytdestruction, nausea, salivation, diarrhoea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity (Shamsuddin M.S.,2016). The high of synthetic activated carbon also make them unaffordable to many people in these countries who live on less than one dollar a day. However, in view of the high cost and associated problems of regeneration, there is a constant search for alternative low cost adsorbents. This difficulty has led to search for the use of cheap and efficient alternative materials such as water hyacinth.

In addition with the above problem, water hyancinth is listed as one of the most productive plants on earth and is considered one of the worlds worst aquatic plants, the weed has in Ethiopia invaded different lakes and rivers including Tana, Awash, Koka and etc. And poses great socioeconomic and environmental problems. Water hyacinth can double its size in 5 days mat of medium sized plants . These dense mats interfere with navigation, recreation, irrigation, power generation and blocks light penetration for submerged or other floating plants that might be present in the water. The blockage of canals and rivers by water hyacinth can cause dangerous flooding.

Water hyacinth can also present many problems for the fish such as decreased fish population, difficult access to the fishing sites and loss of fishing equipment, resulting in reduction in catch and subsequent loss of livelihood. It has been a microorganisms habitat for several diseases causing vectors carrying malaria and river blindness to proliferate.

Physical methods (Mechanical and manual) are short term control measures but a special attention is needed disposing of the plant after mechanical and manual harvesting. Therefore it is necessary to develop a value added product of activated carbon from water hyacinth for aqueous solution treatment of Cr(VI) ion.

In Ethiopia, there exists several indigenous and endemic carbonaceous plants used to synthesis low cost activated carbon for aqueous solution before disposal and wastewater treatment. Of these, water hyacinth that belongs to family abroad world plant with different species used for different purposes. Human beings gathered information by trial and error over centuries. From ancient times human beings uses various plants and herbs that can easily grow in their environment to treat various removal impurities.

1.3. Significance of The Study

This study contributes to reduce the problem occur due to water hyacinth in Awash river. It will play a significant role on environmental and socioeconomic benefits. Water hyacinth causes a major problem like reduction of fish, physical interferences with fishing, obstruction of shipping routes and losses of water in irrigation systems due to higher evaporation. In addition Cr(VI) cause environmental and health problem because it is very harmful even at low concentration and very hazardous cause of their potential toxicity to human and other organisms health. By doing this study, the problem can be decrease. This study focuses on the investigation of low cost activation carbon, characterization, kinetics and equilibrium studies on the water hyacinth stem. Further more, this study provide initial information for the researchers who are interested to conduct further studies on this area.

1.4 Objectives of the Study

1.4.1 General Objective

- ❖ The main aim of this study is to prepare activated carbon from water hyacinth stem and characterize the prepared activated carbon for the removal of Cr (VI) ion from aqueous solutions.

1.4.2 Specific Objective

The specific objectives of the research will be to:

- ❖ Perform the proximate analysis of the water hyacinth stem.
- ❖ Optimize activated carbon preparation parameters such as carbonization temperature, impregnation ratio and holding time.
- ❖ Synthesis activated carbon from water hyacinth (E.C) stem of Awash river by chemical activated method.
- ❖ Examine crystallographic structure and functional group of synthesis activated carbon by using XRD and FTIR techniques respectively.
- ❖ To study the effects of some experimental parameters like pH, initial concentration of Cr(VI), adsorbent dosage and contact time on the percentage removal of Cr(VI) ion by WH stem activated carbon.
- ❖ To study the adsorption isotherm and adsorption kinetics of synthesized activated carbon

2.REVIEW LITERATURE

2.1 Heavy Metals Source And Toxicity

Heavy metals in the environment or toxic metals are trace metals which are detrimental to human health and having a density at least five times that of water (Liu.L.Zhang, 2016). Heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure. Heavy metals are poisonous and destructive contaminants that are released into the environment from the industrial activities (Kamar et al.,2014). They can penetrate into human body via contact, breathing and food consumption (Monachese et al., 2012). Haeavy metals pile up in the soils, water as well as bio-accumulate in living organism without being broken down (Govind and Madhuri, 2014). Bioaccumulation refers to the chemical increase in an organism to the surrounding over time (Kandziora-Ciupa et al., 2017).

Heavy metals affect human beings and animals because they are non-biodegradable. Heavy metal accumulation causes various diseases and disorders (Achparaki et al., 2012). Heavy meatals also form bonds with sulphur groups in the enzymes hence interrupting enzymatic functions and can cause various diseases an disorders (Ojedokun and Olugbenga, 2016, Oves et al., 2016).

Heavy metals form part of the earth's crust where they contribute to the balance of the planet (Vodyanitskii, 2016). Natural activities (weathering and volcanicity) and anthropogenic activities (mining) could be responsible for bringing heavy metals to to the earth's surface from deep earth's crust hence exposing living organism to contamination (Rehman et al., 2018). Once on the earth's surface they can occur in the soils, air, rock and aqueous ecosystems (Shaban et al., 2016). Reported source of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Although, heavy metals are naturally occurring elements that found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds (Liu,L., 2016). Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy

metal pollution (Lu,Y.,2018). Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to less than 10 ppm) in various environmental matrices (Arruti A., 2010).

High level heavy metal contamination of soils is of concern because the metals are able to build up in the food chain thereby causing health risks to human beings. They exist as free ions or organic (inorganic) metal ligands that can either be taken up by plants thereby increasing their chances of entering the food chain (Garbuio et al., 2012 , Akbari et al., 2017). Their toxicity, mobility and solubility can be altered by microorganisms common in the soils (Baran and Tarnawski, 2015).

The microorganisms facilitate mechanisms such methylation, dimethylation and oxidation-reduction processes that transform the toxic substances (Fashola et al., 2016). Methylation by microorganisms is highly preferred in soils of low pH (Frohne et al., 2012). They have the ability to move in the soils. Their movement depends on bonding, metal properties and soil properties (Arshadi et al., 2014).

Polution of water sources is mainly attributed to urbanization, industrialization, agriculture, municipal effluents and increase in population (Waseem et al., 2014, Abbas et al., 2017). Contaminated water is unsuitable for consumption, recreational activities, wild life, industrial use and agriculture (Dipak, 2017). In the aquatic environment, heavy metals occur as colloids, complexes and dissolved ions (Ahenda et al., 2019).

Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation throughout the food chain as non-biodegradable pollutant (Swathi et al., 2014). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before discharge. Widely used heavy metals such as Chromium (Cr), Cadmium (Cd), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb) and Zinc (Zn) are recognized to be toxic in nature (Tahiruddin and Ya'akub, 2013).

2.2 Chromium

Chromium is soft and malleable d-block element with a density of 7.19 g/cm^3 , melting point $1857 \text{ }^\circ\text{C}$ and boiling point $2671 \text{ }^\circ\text{C}$. It is the 21st most abundant element in earth crust and its valence state ranges from -2 to +6 (Agarwal et al., 2011), but the stable forms Cr are the trivalent Cr(III) and hexavalent Cr(VI) species in natural environments, Although there are various others valence states which are unstable and short lived in biological systems. Trivalent chromium occurs naturally in many vegetables, fruits, meat, grains and is often added to vitamins as a dietary supplement, whereas hexavalent chromium, most often produced by industrial processes, mining of chromium ore and aqueous solution of chromium effluent. Cr(VI) is considered the most toxic form of Cr, which usually occurs associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) oxyanions (Kabay et al., 2003). Cr(VI) compounds are found to be more toxic than Cr(III) compounds because of the high solubility, high oxidizing and more mobility in water (Chen et al., 2011).

2.2.1 Chromium Accumulation And Toxicity

Study carried out indicated that accumulation of chromium in four fresh plant species, clams, crabs, and fishes showed that, all four fresh water species and animals were found with high concentration of chromium which is a denotation of its eminent assemblage potentiality (Sarker et al., 2013). Hexachromium moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Govind et al., 2013).

Therefore, the high risk of chromium (VI) is associated with its high reactivity and its potential carcinogenic properties. Acute exposure to Cr (VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems. Ingestion may affect kidney and liver functions (Mandina et al., 2013, Kalandar and Yadav et al., 2014).

It occurs combination with with other elements as chromium salts such as a chromite (FeCr_2O_4), some of which are soluble in water. Chromium (VI) is used in several industrial processes which include: skin tanning, manufacture of stainless steel, electroplating of metals to prevent corrosion, production of pigments, metal alloys, etc. Improper discharge of waste from such processes results to pollution of natural water resources (Sarin and pant, 2016). Cr (VI) is toxic,

can cause genetic change and induce cancer when inhaled (Mebrahtu et al., 2011). Its presence in the environment is of public health concern as it poses danger to aquatic life.

2.3 Water Hyacinth

Water hyacinth (*Eichhornia crassipes*), a common free floating aquatic plant that normally occurs in the form of dense mats, it is a South American native plant that has attained a very broad global distribution in tropical and semi/tropical countries. It grows over a wide variety of wetland types and prefers nutrient/enrich waters. However, it can tolerate considerable variation in nutrients, temperature and pH levels (Amzeze et al., 2014). Water hyacinth is listed as one of the most productive plants on earth, and is considered one of the world's worst aquatic plants. The uncontrolled and fast accumulation of water hyacinth in water causes the stagnation of organic matter in water, blocks the pass of the sunlight that inhibits the photosynthesis process, and decreases the concentration of dissolved oxygen into water.

For the human beings these plants yield health problems, since their roots, stems, and leaves are the habitat of some organism's carriers of severe diseases, such as, encephalitis, helminthiasis, dengue, malaria, and yellow fever, among others. Finally, proliferation of these plants causes water losses due to evapotranspiration, premature drenching of reservoirs, limitation of fishing, navigation and recreational activity, obstruction of irrigation and drainage canals in hydroelectric plants, etc. Therefore, there is a need to manage its spread through suitable control measures (Anah and Astrini, 2018).

To combat the problems caused by the water hyacinth spread, it has been made various efforts to control it. Some of these include weed management methods such as physical removal, chemical (application of herbicides), and release of biological control agents. Since any of these control methods, by itself provides effective results, a logical and site specific integration of different techniques should be desirable.

The constituents of water hyacinth is cellulose (30-50%), hemicelluloses (20-40%) and lignin (15-30%) (Murithi et al., 2014). The cellulose contains functional groups such as O-H, which are involved in adsorption through deprotonation (Anah and Astrini, 2018). Probably, this carbon material has earned this title as result of its characteristics features high surface area, large internal porosity, and amphoteric surface chemistry that have promoted its use in the adsorption

of a lot of adsorbates, such as, volatile organic compounds, dyes, heavy metals, etc. Using of activated carbons for water purification is recognized as a prevailing method, over other purification techniques, and it has become the focus of extensive research because of its simple design, easy operation, low cost, and high efficiency (Anah and Astrini, 2018). During many decades, activated carbon have been produced from anthracite, lignite, petroleum pitches, and other mineral sources, however, during last 20 years, one of the efforts of the scientific production of activated carbons has been focalized on the search of novel eco friendly and low cost raw materials, so that, the use of lignocellulosic resources and waste biomass as precursors has been considered as an important alternative to produce these carbon materials.

Preparation of activated carbon from water hyacinth has two alternatives to mitigate environmental problems of different nature: (a) the presence of heavy metals from water sources and (b) fast proliferation of aquatic plagues.

2.4 Chromium Removal Technologies

Various methods utilized to remove chromium that includes reduction followed by chemical precipitation, electrochemical precipitation, adsorption, ion exchange, reverse osmosis, solvent extraction, membrane separation and etc (Desta et al., 2013). However, most of the physicochemical techniques have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge (Mandina et al., 2013, Khedir et al., 2014). Hexachromium in aqueous solution exists as oxyanions which does not easily precipitate using common conventional precipitation techniques. Ion exchange, reverse osmosis and electro dialysis are efficient for Cr(VI) ions removal but the cost is relatively high. Besides co-precipitation, membrane techniques and solvent extraction are not effective by the removal of metals at their lower concentrations in aqueous solution (Wanees et al., 2012).

On the other hand, adsorption is by far most versatile and effective method for removing any contaminants like heavy metal (Gandhi et al., 2013, Desai et al., 2014). Adsorption by activated carbon prepared from biosorbent has proved to be an economical and effective alternative to conventional metal removal techniques particularly, in treating low concentration of wastewater streams (Garba and Abdullahi, 2016).

2.4.1 Chemical Precipitation

Chemical precipitation is a method, in which dissolved and suspended metal ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates the conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia (Mahmood et al., 2008). Lime is generally used for precipitation purpose due to its low cost and easy control pH in range of 8-10. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of metal and metalloids ions, nature of the oxidation state, pH and presence of complex forming ions, standing time and filtering characteristics of the precipitate (Prathima, 2012; Park et al., 2010).

The removal of Cr (VI) by chemical reduction from industrial waste water involves a two step process: reduction of Cr (VI) under acidic conditions (usually pH 2 to 3) and the precipitation of Cr (III) as hydroxyl species. Besides, gaseous sulphur dioxide, sodium sulfite, sodium metabisulphite, ferrous sulphate, barium sulphite are the most commonly used reducing agent. This technique has been proven as an effective and most widely used to remediate heavy metals including chromium from waste water because it is a simple, inexpensive, convenient, and safe method (Madhavi et al., 2013). However, this technique requires large amount of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes metal precipitation is slow and aggregation take place (Kurniawan et al., 2006).

2.4.2 Reduction

Certain ions such as arsenite, chromate and dichromate have least tendency for precipitation and can not be removed efficiently by any other removal technology. The removal of toxic hexavalent chromium from aqueous solution by biosorption by different biomass types has been extensively reported. This removal is often associated with the simultaneous reduction of Cr (VI) to Cr (III). The biosorption mechanism is a two step process: initiation of the uptake at discrete points by chemical bonding, then reduction of the metal ions (Tsezo et al., 2004).

2.4.3 Ion Exchange

Ion exchange is a suitable technique to remove heavy metal from the wastewater and this technique has also been applied as a remediation measure for Cr (VI) (Nakamura et al., 2017). Various ion exchange resins are commercially available which can effectively remove Cr(VI) below the standard limit of Cr (VI) (0.1 mg/l) in wastewater. This process reduces the amount of waste for disposal and the cost of operation is generally lower. However, the limitation of this method is that efficiency is dependent on the pH of water (Rengaraj et al., 2003).

2.4.4 Solvent Extraction

Solvent extraction is recommended a suitable method for the removal of heavy metals/metalloids from the waste waters of the chemical and electronic industries. Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal/metalloid of interest is mixed intimately with the appropriate organic solvent and the metal passes into the organic phase (El-Hefny et al., 2009). The extraction of Cr(VI) from aqueous solutions of 0.1 M ionic strength by trioctyl methyl ammonium compound, in a mixture of kerosene and xylene indicates that extraction efficiency of Cr(VI) in acidic aqueous solution is good. The removal of arsenic from copper electrolytes by solvent extraction with tributylphosphate has also been reported (Navarro and Alguacil, 1996).

2.4.5 Electrodeposition

Some metals/metalloids found in aqueous solutions can be recovered by electrodeposition technique using insoluble anodes (Issabayeva et al., 2006) reported the electrodeposition of lead and copper ions into palm shell activated carbon electrodes. Cr(VI) removal from an electroplating aqueous solution using the electrochemical precipitation process (ECP). The ECP process was found to be feasible in treating aqueous solution with a high concentration of Cr(VI) (Hansen et al., 2007).

2.4.6 Electrodialysis

Electrodialysis is accomplished by placing cation and anion selective membranes alternatively across the path of an electric current (Ribeiro et al., 2000). When current is applied, the electrically attracted cations pass through the cation-exchanging membranes in one direction and the anions pass through the anion-exchanging membranes in other direction. The result is that salinity decreases between one pair of membranes and increases between the next pair. Water can then pass through several such membranes until the required salinity is removed (Paul et al., 2007). Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation.

2.4.7 Adsorption

Adsorption is the process in which different molecules, ions and atoms of liquid or gas get attached to the surface of the solid. Adsorbate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate, which is usually in the form of fluid, percolates in to the absorbent (Gisi and Lofrano, 2016). Thus, absorption includes the whole matter whereas adsorption is only effective on surfaces. However, both terms are included in a single term called sorption and the reverse is called desorption. Thus, in the process of adsorption, the substance is separated from fluid phase and is accumulated on the solid phase substrate (Suteu et al., 2015).

Adsorption offers significant advantages like low cost, availability, profitability, ease of operation and efficiency in comparison with the conventional methods especially from economical and environmental point of view. The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and adsorption using activated carbon as adsorbent has been frequently used (Madhavi et al., 2013).

Typical biosorbents can be obtained from various source of non-living biomass like, wool, olive, cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used tires, soot, hazelnut shell, banana peel, sea weed, dead fungal biomass, cyan bacterium, green alga and etc have been used for the removal of chromium from waste water and aqueous solution. These materials can be used as adsorbents with little processing and locally available in large quantities (Tahiruddin and

Ya,akub, 2013). In adsorption, the solute present in dilute concentration in liquid or gas phase is removed by contacting with suitable solid adsorbent so that the transfer of the component first takes place on the surface of solid and then into the pore of the solid.

This is an economic, environmental friendly method of removing heavy metals from waste water and aqueous solution. It involves movement of substance from liquid phase to solid phase. The transferred substance is bound by chemical or physical interactions (Tripaathi and Manju, 2015). Adsorption mainly is used in purification of gases or liquid. The adsorbing material is known as adsorbent. The material being adsorbed is called adsorbate (Tripathi and Manju, 2016). In chemical adsorption the adsorbate and adsorbent react (Hegazi, 2014). The interaction between the two is characterized by strong covalent or ionic bond. The chemical adsorption is also called chemisorption while physical adsorption is also called physisorption (Gisi et al., 2016).

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. The process is influenced by many physicochemical factors such as sorbent surface area, particle size, temperature, pH, contact time and sorbent interaction (Suteu et al., 2015). It is customary to divide adsorption in to two broad classes, namely, physical and chemical adsorption (Ong and Khoo, 2011).

2.4.7.1 Physisorption

Physisorption or physical adsorption occurs when energy difference and electrical attractive forces (weak van der Waals forces), adsorbate molecules become physically fastened to the adsorbent surface. Physisorption takes place with the formation of single or multiple layers of adsorbate on the adsorbent surface and characterized by low activation energy of adsorption (Beyene, 2014). So

1. Physical adsorption is believed as a result of van der Waals forces between the adsorbate and adsorbent and usually associated with low heats of adsorption.
2. Physical adsorption equilibrium is attained very rapidly (except when limited by mass transport rates in the gas phase or within a porous adsorbent).

3. Physical adsorption is reversible means the existence of adsorption desorption equilibrium.
4. Physical adsorption does not stop a monolayer formation but may advance into multilayer adsorption.

2.4.7.2 Chemisorption

Chemisorption or chemical adsorption occurs when a chemical action occurs between the adsorbed molecules and the adsorbent. Chemisorption takes place with the formation of a single layer of adsorbate attached to the adsorbent surface by chemical bonds. This type of interaction is strong with a covalent bond between adsorbant and the surface of the adsorbent is characterized by a high enthalpy of adsorption (Beyene, 2014).

1. Chemisorption may be rapid or slow and occur in high heats of adsorption.
2. In chemisorption, the certain chemical bonding is formed between the adsorbent and the adsorbate molecules.
3. There is generally no adsorption-desorption equilibrium in chemisorption.
4. Because of chemical bonding, chemisorption is expected to be a monolayer of molecules on the adsorbent.

The general features which distinguish physical adsorption from chemisorption are as follows

<u>Physical adsorption</u>	<u>Chemisorption</u>
Low heat of adsorption	High heat of adsorption
Non-specific	Highly specific
Monolayer or multilayer	monolayer only
No dissociation of adsorbed species.	May involve dissociation.
Only significant at relatively low temperatures.	Possible over a wide range of T
Rapid, non-activated and reversible.	Activated, may be slow and irreversible

No electron transfer although-
polarization of sorbate may occur.

Electron transfer leading to bonded formation
between sorbate and surface.

Even so, there is no sharp dividing line between these two types of adsorption there are cases of adsorption possessing characteristics which are intermediate between physical adsorption and chemisorption.

2.5 Mechanism of Adsorption

Among the unit operations aqueous solution treatment, adsorption occupies an important position since it is an efficient and economically feasible process for treatment of aqueous solution containing dissolved pollutants (Ayala, 2016; Jemal, 2015). In the adsorption process, the molecules are extracted from one phase (liquid) and concentrated at surface of secondary phase (solid phase adsorbent) which occurs due to an attractive force existing between the adsorbent surface and the adsorbate molecules. Therefore, it is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction. The adsorption process consists of three consecutive steps (Mohammed, 2011).

- Substances adsorb to the exterior of the adsorbent
- Substances move into the adsorbent pores
- Substances adsorb to the interior walls of the adsorbent

While adsorption is the phenomena of accumulation of a large number of molecular species at the surface of solid or liquid phase in comparison to the bulk. When the molecules in the liquid phase (sorbate) become attached to the surface of the solid phase (adsorbent) as a result of the attractive forces at the adsorbent surface overcoming the kinetic energy of the adsorbate molecule (Okmen et al., 2011).

2.6 Adsorbents for Chromium Removal

Virtually every solid surface has the capacity to adsorb sorbate but the effectiveness of these solids in the aqueous solution treatment process are a function of its structure, degree of polarity, porosity and surface area. The adsorbate may be an organic compound with undesirable properties such as color, odour, etc. The principal types of adsorbents include activated carbon, organic polymers and silica-based compound (Mohammed, 2011). These include activated carbon, silica gel, zeolites, clay, nanoparticles, biological wastes, exchange resins and low cost activated carbon.

2.6.1 Commercial Activated Carbon

Activated carbon (AC) is solid, porous, black carbonaceous material. It is main adsorbent used in industries in the activated carbon. It can be prepared from a large number of sources such as coconut shells, peat, black ash, charcoal, lignite, bituminous coal, petroleum coke and etc. Any carbon source can be converted in to activated carbon via a number of methods. Different physical forms of activated carbon are produced depending on their application among these forms, the two most common forms are granular (GAC) forms to be used in adsorption columns and powder (PAC) forms use in batch adsorption followed by filtration (Allen and koumanova, 2005). Activated carbon has high internal surface area and pore volume which make it very convenient to be used as adsorbent, catalyst or catalyst supports in gas and liquid phase processes for purification and chemical recovery (Radovic et al., 2011).

Activated carbons are high surface area and porous carbon has been widely used as an adsorbent for separation, purification, decolorization and deodorization of vegetable oils and fats, water purification and pollution treatment, air and gas purification and the food and pharmaceutical industries. Activated carbon is widely used for the purpose due to the large surface area available for adsorption or chemical reactions as a result of its high degree of micro porosity (Abbas, A.F., 2016). The importance and relevance of activated carbon to an ever growing society can not be overemphasized considering its enormous uses (Gonzalez-Garcia,P., 2018).

The process of adsorption on activated carbon of Cr(VI) ion with cellulose is interesting due to its abundant availability and its great potential in removing heavy metals present in

water, demonstrating in experimental processes in the treatment of water (Chitpong et al. 2017). The presence in the cellulose of hydroxyl (OH), amino (NH₂), and carboxyl (C=O) groups facilitate the adsorption of heavy metals through cation exchange (Lin et al. 2018; Anirudhan et al. 2016). Nowadays, almost all adsorbents are developed for the removal of heavy metal ions and based on the interaction with the functional groups that are present in the adsorbents .

However, these high technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, results in loss of the adsorbent, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal (Ruan et al. 2016). This has led many workers to search for more economic adsorbents.

2.6.2 Non-conventional Low Cost Activated Carbon

Due to the problems mentioned above, study interest in to the production of alternative sorbents to replace the costly activated carbon has intensified in receny years. Attention has focused on various natural solid supports, which are able to remove pollutants from aqueous solution at low cost. Cost is actually an important parameter for comparing the adsorbent material. Researchers are in a hunt for developing more suitable, efficient, cheap and easily available types of adsorbents, particularly from waste materials (Bharathi and Ramesh, 2013). So, environmentally friendly processes need to be developed to clean-up the environment without creating hazard waste by-products (Sen and Dastidar, 2010). Low cost activate carbon has several advantages over other techniques ,including stability and reusability of the solid phase, easiness of separation and enrichment under dynamic conditions, no need for organic solvents and minimal costs due to low consumption of reagents (Soliman and Ahmed, 2010).

Recently some natural materials had been used as adsorbent for heavy elements from aqueous solutions such as wheat bran (Nameni et al.,2008), potato peel waste (Abdullah and Devid Prasad, 2009), volcanic ash soil (Babel and Opiso,2007), powder of potato peelings (Mutongo et al.,2014), Leaves of *Euclea schimperi* (Gebrehawaria et al.,2015).

2.7 Preparation of Activated Carbon

Activated Carbon (AC) does not just happen; it has to be synthesized. The porosities of a carbon, as initially prepared by carbonization are not sufficiently developed for most application. Activated carbon can be synthesized by two methods, physical and chemical activation.

2.7.1 Physical Activation

Physical activation method consists of carbonization of the precursor material in an inert atmosphere and gasification of the resulting char in the presence of steam, carbon dioxide or air (Liu, Y., 2016). Physical activation is a two step process. It involves carbonization of raw material followed by activation at elevated temperatures in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures for activation temperature ranges between 400 C⁰ to 800 C⁰. Generally, CO is used as activation gas, since it is clean, easy to handle, and it facilitates control of the activation process due to slow reaction rate at high temperatures. The precursor is usually subjected to carbonization followed by activation or using either.

2.7.1.1 Carbonization

The method of production of the carbonized intermediate product has a marked effect on the quality of the final activated carbon product. The main aim of carbonization is to reduce the volatile content of the source of material in order to convert it to a suitable form for activation. During the phase of the carbonization, carbon content of the product attains a value of about 80 percent. By carbonization most of the carbon elements hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material and the freed atoms of elementary carbons are grouped into organized crystallographic formation known as elementary graphitic crystallites (Balcf, 1992).

Carbonization is the first stage where the precursor is pyrolyzed in the temperature range 600-900 °C, in an inert atmosphere (nitrogen, argon) resulting in the formation of char, which is normally non-porous.

In the simple carbonization product, the mutual arrangement of the crystallites is irregular, so that free interstices remain between them. However, as a result of deposition and decomposition

of tarry substances, these become filled crystal blocked by disorganized (amorphous) carbon. The resulting carbonized product has small adsorption capacity. Such carbonized materials can then be partially activated by removing the tarry products by heating them in a stream of an inert gas, or by extracting them with a suitable solvent, or by a chemical reaction.

2.7.1.2 Activation of Carbonized Intermediate Product with Gaseous Agents

A carbon with a large adsorption capacity can also be produced by activating the carbonized material under such conditions that the activating agent reacts with the carbon. The most common activation agents are steam, carbon dioxide and oxygen (air). The activation step is generally conducted at temperatures 500_1100 °C. The active oxygen in the activating agent basically burns away the more reactive portion of the carbon skeleton as carbon monoxide and carbon dioxide, depending on gaseous agent employed.

The main factors that influence that rates of the reaction of carbon with carbon dioxide, steam and oxygen are: i) the concentration of the active sites on the carbon surface, ii) the crystallinity and structure of the carbon, iii) the presence of inorganic impurities and iv) the diffusion of reactive gases to the active sites.

2.7.2 Chemical Activation

In chemical activation the precursor is impregnated with a given chemical agent and pyrolyzed after that. As a result of the pyrolysis process, a much richer carbon content material with a much more ordered structure is produced and once the chemical agent is eliminated after the heat treatment, porosity is highly developed.

In chemical activation the starting materials is impregnated with a strong dehydrating agent and then followed by pyrolysis at high temperature to prepare activation carbon. In chemical activation process, the precursor is mixed with a chemical agents such as sulphate salts, chloride salts, KOH, HCL, ZnCl₂, H₂SO₄, H₃PO₄ carbonized and washed to produce the activated carbon (Bhatnagar, A., 2013). An important advantage of chemical activation is the process normally takes place at lower temperature (400 °C_900 °C) and for a shorter time than those used in physical activation. In addition, very high surface area activated carbons can be obtained.

Moreover, the yields of carbon in chemical activation are usually higher than those in physical activation because of chemical agents used are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of the other volatile products. On calcination, the impregnated chemicals dehydrate the raw materials, which results in changing aromatization of the carbon skeleton by the creation of a porous structure and surface area.

The material mainly used in the production of activated carbon consists predominantly of cellulose, and therefore in a discussion of the mechanism of chemical activation the action of chemical agent on cellulose must first be considered. Simultaneously hydrolytic or oxidative reactions take place, by which the macromolecules are gradually depolymerized (Browning, 1963, Cerny, 1970). The activated carbons produced through chemical activation, one advantage of using phosphoric acid as activating agent is easily cleaned from the activated carbon by rinsing with boiling pure water (Yagci 2004).

2.8 Factors Affecting Adsorption of Cr(VI) Ion

Many physicochemical factors influence the amount of adsorption of an adsorbate (Cr(VI)) ion onto an adsorbent include surface area of adsorbent, initial Cr(VI) ion concentration, temperature, pH, contact time and adsorbent dosage etc. (Salleh et al., 2011).

2.8.1 The effect of Initial Chromium Concentration

The initial chrome concentration is important in adsorption, since a given mass of sorbent material can only adsorb a fixed amount of metal. The effect of initial Cr(VI) ion concentration relies on the immediate relation between the Cr(VI) concentration and the available binding sites on the adsorbent surface. Normally percentage removal of chromium will decrease with increase in chrome concentration, this is because for a given mass of adsorbent material; the amount of chrome that can be adsorbed is fixed. The higher concentration of chrome, the smaller amount can remove. At a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial chrome concentration increases, the active sites required for adsorption of the chrome will be lacking.

2.8.2 Effect of Solution pH on Adsorption

The pH seems to be the most important parameter for removal of Cr(VI) from aqueous solution by activated carbon (Tang et al., 2009). It affects the solution chemistry of the metal and the network of charges on the surface of the sorbent, as well as physico-chemistry and hydrolysis of the metal (Collins and Stotzky, 1996). The pH value of the solution will determine the surface charge of the adsorbent, which will affect the interaction between the adsorbate and adsorbent. The pH of the system exerts profound influence on the adsorption uptake of adsorbate molecules most probably due to its influence on the surface properties of adsorbent and ionization or dissociation of the adsorbate molecule (Santhi et al., 2010). The pH of the aqueous solution plays an important role in the whole adsorption process and particularly on the adsorption capacity of adsorbent. The rapid decrease in the removal of Cr(VI) with the increase of pH may be due to that low pH leads to an increase in H⁺ ions on the carbon surface, which results in significantly strong electrostatic attraction between HCrO₄⁻ and positively charged carbon surface (Bhatti et al., 2007). The acidity of solution, influencing not only the surface charge of the adsorbent and the degree of ionization of the material present in the solution, but also the solution chemistry of adsorbent (Jafari and Ahmady Asbchin, 2012).

2.8.3 Effect of Contact Time

The adsorption of Cr(VI) on any activated carbon was rapid initially and with further increase of time the adsorption kinetics decreased, and finally reached equilibrium.

2.8.4 Effect of Adsorbent Dose

The Cr(VI) removal efficiency was found to increase with the increase of adsorbent dose in various studies and after reaching the optimum value, further increase in adsorbent dose does not shows any significant change (Dubey and Gopal, 2007). The trend of increase in removal capacity is due to the fact that the availability of more adsorption sites for the metal ions (Mohanty et al., 2005).

2.8.5 Effect of Temperature

Process temperature has a profound effect on heavy metal removal by using various adsorbent and the optimum temperature for better removal changes with the type of adsorbent and adsorbate. With the increase of temperature the uptake of Cr(VI) increases continuously (Barkat et al., 2007). The adsorption of Cr(VI) on activated carbon increases as the temperature increases and thus the adsorption reaction is endothermic in nature (Kartikeyan et al., 2005). The enhancement of adsorption capacity may be due to the chemical interaction between adsorbate ions and adsorbent, creation of some new adsorption sites or increase in the intraparticle diffusion of Cr(VI) into the pores of adsorbent at high temperatures (Namasivayam and Yamuna, 1995). The more increase in temperature, the higher the removal rate with respective optimum temperatures.

2.9 Characterization of Activated Carbon

Characteristics of activated carbon depend on the physical and chemical properties of the raw materials as well as method of activation (Abechi,S.E,2013). Preparation and characterization of activated carbon prepared from balsamodendron caudatum wood waste through various activation processes. They were prepared activated carbon from wood waste by various chemical processes. The scanning electron microscopy were used for study of morphology and the surface functional group was investigated by Fourier transformation infrared spectroscopy techniques. Physico-chemical characteristics such as bulk density, moisture content, ash content, matter soluble in water, matter soluble in acid, pH, iodine number, conductivity, porosity, yield percentage and surface area was carried out to assess the suitability of the carbon as adsorbent (B.Sivakumar, 2010).

Preparation and characterization of activated carbon from Lapsi Seed Stone by chemical activation with Potassium Hydroxide. Prepared activated carbon was characterized by pH, moisture content, Fourier transform-infrared spectroscopy, scanning electron microscopy methylene blue and iodine number (Sahira Jobsi,2013). Synthesis and characterization of activated carbon from Saudi Arabian Dates Tree's studied characteristics of activated carbon by using techniques like infrared spectroscopy transmission electron microscopy, scanning electron

microscopy, X-ray diffraction, optical microscopy, apparent surface area estimation by nitrogen adsorption iodine number and ion-exchange capacity (Hassan M.Al-Swaiden ,2015). Production and characterization of activated carbon from Snail Shell waste studied by characteristics of produced activated carbon such as pH, pore volume and porosity, ash content, determination of moisture content, bulk density and the activated carbon prepared was characterized, showing effect of temperature on ash content, pore volume and porosity (Rhoda Habor Gumus, 2015).

Preparation and characterization of activated carbon from green coconut shells by chemical activation method was characterized by XRD, SEM, FT-IR and TG (Dipa Da, 2015). Preparation and characterization of activated carbon from rice husk characterized by SEM, in order to identify the functional group responsible for adsorption Fourier transform infrared spectroscopy analysis was carried out. BET surface of both samples were identified using nitrogen adsorption-desorption isotherms, along with this pore size, pore volume created in samples were also identified (Hariprasad.P, 2016).

Preparation and characterization of activated carbon derived from *Borassus flabellifer* flower as electrode material for super capacitor applications. There were used *Borassus flabellifer* flower for the preparation of activated carbon activated by using H_3PO_4 as an activating agent. Scanning electron microscopy-ray analysis and Fourier infrared spectroscopy analysis were used for activated sample analysis (M.Sivachdambarame, 2017). Characterization of activated carbon and application of chromium removal from aqueous solutions. The remove of chromium ions from aqueous solution by adsorption using Granular activated carbon which was characterized using nitrogen porosimetry, pH titration, Boehm's titration, mercury porosimetry, FT-IR and scanning electron microscope measurement(Yasemen Kutmen,2007). The proximate analysis including moisture content, ash content, bulk density, pH , and pH at zero charge was conducted to identify the psychochemical properties of the adsorbent (Riry Wirasnita , 2015).

The preparation conditions were varied to study their effects on the surface area, porosity, morphology, functionality and crystal structure.They were studied variables like time of carbonization, time of activation, activating agent, particle size, sample pre-drying, hydrogen peroxide post treatment and the effect of the activation process (Amjad H.,2014).

2.10 Equilibrium Adsorption Isotherm Models

Depending on both the nature of the adsorbent and the interaction type, various kinds of isotherms can be distinguished. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e , to the concentration of the solute in the liquid, C_e , with which it is in contact. The adsorption isotherm is also an equation relating the amount of solution adsorbed on the solid and the equilibrium concentration of the solution at a given temperature (Gonen and Serin, 2012).

The relationship between these q_e and c_e can normally be fitted to one or more equilibrium isotherm models. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. The most commonly used isotherms for the application of activated carbon in aqueous solution treatment are the Langmuir and Freundlich isotherms. Freundlich is only applicable to physical adsorption while Langmuir is applicable to chemisorption.

2.10.1 Langmuir Isotherm Model

Langmuir isotherm which is based on monolayer coverage prediction of the adsorbate, this model also suggests that there is no lateral interaction between the sorbed molecules. It assumes that the adsorption takes place at specific homogeneous sites within the adsorbent with no lateral interaction between the sorbent molecules (Sivanesan V., 2005). The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface (adsorption occurs at specific homogeneous adsorption sites), that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The model is based on the following assumptions.

- i. Adsorbate molecules are attached to the surface of the adsorbent at definite localized sites.
- ii. Each site can hold one adsorbate molecule
- iii. All adsorption sites are energetically equivalent
- iv. The interactions between the adsorbed molecules are negligible.

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b C_e q_m} \text{-----(2.1)}$$

Where, q_e is the amount of adsorbate adsorbed per unit amount of adsorbent (mgg^{-1})

C_e is the equilibrium concentration (mg l^{-1})

b Langmuir equilibrium or adsorption constant (L mg^{-1}) and

q_m is Langmuir monolayer saturation capacity (mgg^{-1}).

Essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1 + b C_0} \text{----- (2.2)}$$

Where, C_0 is the initial concentration of Cr (VI) ions (mg /L)

b is obtained from slope of Langmuir plot.

Table 2.1 . Types of isotherm for various R_L

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

(Cabuk *et al.*, 2007)

2.10.2 Freundlich Isotherm Model

The Freundlich equation is basically empirical, but is often useful as a means for data description. Assumes adsorption occurs at heterogeneous surface or surfaces supporting site of varied affinities (Langmuir J. Am. 1918).

The Freundlich Linearized equation

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \text{-----(2.3)}$$

Where q_e is the amount adsorbed at equilibrium (mg/g)

k_f is constant that describes the adsorption capacity of the adsorbent (mg /g)

n is empirical parameter that dictates the intensity of the adsorption.

$1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption

C_e is the equilibrium concentration of chromium (mg/L).

The values of k_f and n can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$ of the Freundlich Plots. The Freundlich isotherm basically indicates whether the adsorption proceeds with ease or difficulty. Where n is dimensionless, represents Freundlich constants characteristics of the system and the measure of the nature and strength of the adsorption process and the distribution of active sites.

Table 2. 2 Freundlich Constant Characteristics (N)

N	Strength of the bond energy sorption process
$n > 1$	Decreases with surface density
$n < 1$	Increases with surface density
$n = 0$	All surface sites are equivalent
$1 < n < 10$	Beneficial sorption

(Febrianto *et al.*, 2009)

2.11 Kinetics Studies

The kinetics of metal ion sorption has been described as a very important parameter for designing sorption systems. A rapid kinetics will facilitate smaller reactors while a slow rate of uptake will require long columns to utilize maximum potential of the biosorbent. The rate of sorption onto a sorbent surface depends on a number of factors such as structural properties of the sorbent, initial concentration of the solute and the interaction between the solute and the active sites of the sorbent (Vinodhini and Das, 2010).

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{-----} \quad (2.4)$$

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad \text{-----} \quad (2.5)$$

$$q_e = k_w t^{0.5} \quad \text{-----} \quad (2.6)$$

where, k_w is intra particle diffusion rate constant (mgg⁻¹min^{0.5}), q_t is amount of adsorbate adsorbed on adsorbent at constant time t (min), k_1 and k_2 are equilibrium rate constant of pseudo-first and second -order adsorption (min⁻¹).

3. MATERIALS AND METHODS

3.1. Chemicals And Instruments

Different types of materials and chemicals was used during the synthesis, characterization, equilibrium and kinetics studies of low cost activated carbon from water hyacinth stems span of the experimental works.

3.1.1. Instruments and Equipments

The instruments used for this study were; Infrared spectra of water hyacinth before and after Cr(VI) adsorption were obtained using FT-IR Model JASCO (Japan) in the range 4000-400 cm⁻¹ used to characterize the functional group of activated carbon made from water hyacinth. Jenway pH meter Model 3510 to adjust the solution pH to the desired point. Flocculator lovibond instrument (Germany) which used for mix the material with a solution at 150 rpm for varied times.

Uv-visible Spectroscopy (Lambda 35 Ferkin Elmer) used to determine the absorbance of Cr(VI) ion concentration after batch adsorption, Rotary shaker (Orbital shaker SOL,UK) to agitate the sample, FTIR Spectrometry (presige 21) to detect functional groups, Electronic balance (OHAUS, Swizerland) for weighting, Erlenmeyer flasks (Germany), XRD, Volumetric flasks (PYREX,UK), Electrical mill (IKA WERKE) or mortar used to grind water hyacinth stem, Whatmann No-1 filter paper (125mm) used to separate the residue from the solution after the experiment. Sieve to get 1mm particle size, Hot Air Oven (Contherm 260M) to dry sample, deionizer, fridge, Buchner flask, funnel, Porcelain crucible used for sample handling during carbonization. Muffle furnace (Nabertherm B180, Germany) was used for the purpose of activated carbon, volatile matter and ash content determination. Aluminium foil, 250 mL conical flasks, test tubes, beakers.

3.1.2. Chemicals and Materials

Water hyacinth stem (collected from Awash river) was used for activated carbon. All the chemicals used were of analytical grade: potassium dichromate (K₂Cr₂O₇ 99.5%) was used as

prepared adsorbate and working solution, 30% H_3PO_4 was used as dehydrating or chemically activating the raw water hyacinth. Deionized water used for sample preparation, for dilution of the reagents and rinsing purposes. 0.1 M hydrochloric acid (95% HCl) and 0.1 M Sodium hydroxide(NaOH) was used to adjust the pH of the solution (Riedel-deHaen, Germany). Buffer solutions (pH =4, pH=7, pH=10) to calibrate pH meter. All the chemical reagent will be purchased from the chemical markets in Ethiopia. Potassium dichromate ($K_2Cr_2O_7$) was used as adsorbate. Doubly distilled water was obtained from our lab.

3.2 Experimental Methods and Procedures

3.2.1 Raw Material Preparation

Water hyacinth plants (*Eichhornia crassipes*) utilized for the preparation of adsorbents was procured randomly from the local fields in Awash river Awash Zone in Oromia, Ethiopia, which 247 km far from Debere Berhan in July, 2020. The stems (petioles) were separated from other parts and were thoroughly washed with tap water for several times to remove soil ,dust and other impurities. It was then washed with distilled water several times. The separated water hyacinth stems were cut into small pieces and dried by sun light for a week and then dried in an oven at $105\ ^\circ C$ for 24 hours to remove moisture. Water hyacinth stem was selected for the preparation of activated carbon.



Figure 3. 1 Pretreatment of water hyacinth

3.2.2 Preparation of Activated Carbon

There are basically two methods for manufacturing activated carbon, i.e physical and chemical activation. In this study chemical activation was used for the preparation of activated carbon.

Activated carbon was prepared using the chemical activation method according to the procedure by (El-Demerdash et al. 2015) with some modifications. The dried stems were ground to fine powder and sieved through a standard sieve (Sonar GSMS) to obtain particles size of 300 microns (0.3 mm) and stored in sample holder till used in experimental purposes. The sieved samples were then impregnated into three times its wt. (1: 3) with concentrated solution of phosphoric acid (30%) for 24 hours and filtered by suction filtration through washed by distilled water to remove the color, impurities and excess residual acid (Daniel Kibami, 2015). Then oven-dried at 105 °C for 12 hours were dried before carbonization. The activation /carbonization was done at 550 C⁰ for 1:30 hours using a muffle furnace the samples were heated gradually in absence of air. After cooling to room temperature, the activated carbon obtained was washed thoroughly with distilled water until the pH of the supertant (effluent) become steady at about neutral. After that, the samples were dried at 105 °C for 12 hr. Finally, the low cost activated carbon prepared from water hyacinth stems (SWH) were ground and stored in prepared sample holder till used in for further studies.



Figure 3. 2: Water hyacinth stem activation

3.3 Characterization of the Prepared Activated Carbon

3.3.1 FT-IR spectroscopy

FT-IR is one of the key tools used to characterize the functional groups the surface of the carbon. Water hyacinth low cost ACs and metal loaded water hyacinth low cost ACs samples were prepared differently and scanned for various functional groups in the spectral range of 400-4000 cm⁻¹ using the FTIR (Model: IR Affinity 1S class 1).

3.3.1.1 FTIR of water hyacinth stem activated carbon

Spectra analyse was done for water hyacinth stem activated carbon transform infrared spectrometer (FT-IR). In this analysis, a tablet form of the sorbent was put in the sample disks

then measured the spectra of the activated carbon. The sample was placed on 7mm collar and pressed to form a pellet by putting the set of metal die and a screw together. The collar containing the pellet was removed from metal die and a screw and it was placed in a cuvette. The machine was switched and the sample was scanned. Various bands in the spectrum were identified as corresponding to different bonds in different functional groups.

3.3.1.2 FTIR of metal loaded water hyacinth stem activated carbon

The water hyacinth stem residue after adsorption and filtration was further oven dried at 105 °C for a day to remove moisture completely. 0.5 g of dry fractions of metal loaded water hyacinth were ground into powder using mortar and pestle. 1.0 g analytical grade KBr was mixed with the fine powder using a mortar. The mixture was fine ground. The sample was placed on 7 mm collar and pressed to form a pellet by putting the set of metal die and a screw together. The collar containing the pellet was removed from metal dye and was placed on the sample holder. The machine was switched on and the sample was scanned. The spectra were compared with that of water hyacinth ACs.

3.3.2 Preparation of Adsorbent

All plastic bags, polyethylene bottles, plastic bottles, plastic scoops and glass wares was thoroughly washed with detergent, rinsed with water and then with distilled water before soaking into 30% H₃PO₄ for about 24 hours. Containers was finally rinsed with deionized water before being used for sampling.

Above raw material of about 110 gram was impregnated with activating agent H₃PO₄ 100 ml of different concentrations 10, 20, 30, 40 and 50% was used. The pieces were soaked in a solution of 30% phosphoric acid (H₃PO₄) at 1:3 (w/w%) impregnation ratio for 24 hr at room temperature. Pyrolysis treatment (activation) step was performed as follows: about 110 g of the water hyacinth stem pieces per partition was placed in pre-weighed glass crucibles and carbonized in a muffle furnace for 1.30 hr in the absence of oxygen at different temperatures, 200, 300, 400, 500, 600, 700, 800 and 900 C⁰ respectively. The resulting carbonized samples were cooled to room temperature under inert atmosphere and was ground into powder and washed with 1L of deionized water to remove residual acid using a Buchner flask and funnel. Finally, the activated

carbon was dried at 105 °C for 2:30 in an oven and sieved with 150 micrometer mesh size to obtained fine powder of activated powder. The powdered activated carbon was kept in air-tight containers and used when required.

3.4 Preparation of Adsorbate Solution (Synthesized Solution)

A stock chromium solution of 1000 mg/L was prepared by dissolving an 2.875 gram of chromium dichromate (Cr) in a 1 L of distilled water in volumetric flask and making diluted to the mark with double deionized water to avoid errors in the results. The pH meter was calibrated with Orian standard buffers before any measurements

The working solutions were prepared through serial dilutions of the stock solution. The working solutions were prepared by diluting the stock deionized water to give the required concentrations of the working solutions in 250 ml Erlenmeyer flasks. Six different concentrations of the adsorbate will be prepared as 10, 20, 30, 40, 50 and 60 ppm. The metallic concentrations of the working solutions prepared were based on the concentration of the same stock solutions at each steps wise by dilution law equation.

$$C_1V_1=C_2V_2 \text{ -----(3.1)}$$

Where C₁- concentration of the stock solution

C₂- concentration of intended to be made

V₁- volume to be taken from the stock solution

V₂- volume intended to be made

3. 4.1 Calibration of Cr(VI) Ion Absorbance

To calculate the Cr(VI) concentration from each batch adsorption experiment, a calibration curve was first prepared by using the standard Cr(VI) solution with known concentrations. Different concentrations (0, 10, 20, 30, 40, 50 and 60 mg/L) were prepared and absorbance values were recorded using Uv/Vis spectrometer. These concentrations were taken based on the final

concentration of Cr(VI) after adsorption. Calibration curve of this data is served the basis for determining the Cr(VI) concentration variation as a result of the Cr(VI) adsorption process during the experimental work.

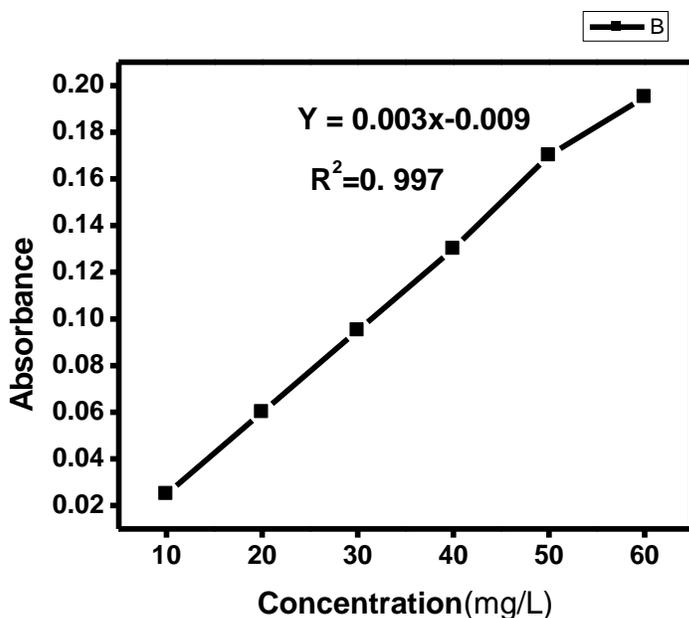


Figure 3. 3 Calibration Curve for Cr(VI) ion versus Absorbance

3.5 Batch Adsorption Experiments

All the adsorption experiments were carried out at constant room temperature in an environmental incubator shaker at constant shaking speed of 200 rpm. Concentration of hexavalent chromium in each solution was determined by Uv/Vis absorption spectrometer. Adsorption of Cr(VI) on developed ACs was conducted with 100ml of solution taken into 250 ml Erlenmeyer flasks by varying different parameters such as (2.0 _10.0), initial Cr(VI) concentration (10, 20, 30, 40, 50, 60) ppm and adsorbent dose (0.5, 1, 1.5, 2.0, 2.5, 3.0) gram. Batch adsorption experiments performed by contacting 2.0 gram of the selected carbon sample with 100 ml of the aqueous solution of different initial concentrations and pH values. All the experiments were carried out in triplicate and the mean values were considered.

Adsorption equilibrium isotherms on the prepared ACs were determined using sample dosage of 2.0 gram, initial concentration Cr(VI) of 50 ppm and at different pH values. pH values were adjusted with 0.1 M HCl and 0.1 M NaOH solutions by using pH meter.



Figure 3. 4 (a) working solution (b) optimization

3.5.1 Factors Affecting The Batch Equilibrium Studies

Batch experiment was carried out to find the optimum pH, contact time, thermodynamic studies, equilibrium isotherms and kinetic studies.

The effects of solution pH, initial copper concentration, contact time, adsorbant dosage and solution temperature on the up take of chromium onto the AC was investigated. Sample solutions was withdrawn at predetermined time interval, filtered through a 0.150 mm pore size membrane and the residual concentration of the chromium ion was then analysed by Uv-Visible spectrophotometer. Equilibrium studies was carried out by varying initial Cr (VI) concentration (10, 20, 30, 40, 50 and 60 mg/L) with a working volume of 100 ml. Experiments are doing in triplicates and average of data obtained will be calculated. The amount of adsorbate (metal ion) adsorbed at equilibrium, q_e (mg/g) and the percentage removal (efficiency of adsorption) was calculated by using the following equation:-

$$q_e = \frac{(C_0 - C_e)V}{W}, \text{----- (3.2)}$$

$$\% \text{Removal} = \frac{(C_o - C_e)100}{C_o} \text{-----} (3.3)$$

Where C_o and C_e (mg/L) are the initial and equilibrium sorbate concentrations, respectively. W is the mass of adsorbent (g) used and V is the volume of the solution (L).

To study the effect of initial Cr(VI) concentration and contact time on the adsorption uptake, 250mL of adsorbate solution with known initial chromium concentration (10-60 ppm) was prepared in a series of 250 mL conical flasks and 1.0 g AC was added in to each flask. The flasks was covered with aluminium foil and placed in an isothermal water bath shaker at constant temperature of 25 °C with rotation speed of 200 rpm for 24 hr. For study on effect of solution pH on the chromium ions, the adsorption process was studied by varying the solution pH from 2.0 to 12.0. The pH was adjusted by adding 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH), and was measured by pH meter. The effect of adsorbent dosage was studied by adding an adsorbent dosage from 0.5 to 2.5 g to a 100 mL solution containing 50 ppm of the metal ions at optimum pH. To ensure reproducibility and accuracy, each batch adsorption experiments was performed in triplicates.

3.5.2 Effect of Contact Time

Contact time is one of the most important parameters for the assessment of practical application of adsorption process (Shan *et al* 2007). For the determination of the rate of Cr(VI) ions adsorption by the low cost activated carbon of water hyacinth stems from 50 mL of standard solutions, the quantity of metal ions adsorbed was determined by varying the contact time: (30, 60, 90, 120 and 150 min). Other parameters were kept constant.

3.5.3 Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied by using 0.5, 1.0 , 1.5 , 2.0 and 2.5 g of water hyacinth stem in 250 mL Erlenmeyer flasks with metal ion concentration of 50 mg/L and the adsorption efficiency for different doses was determined by keeping other parameters constant (Kilic et al. 2011).

3.5.4 Effect of pH

The effect of pH on adsorption of metal ions was studied within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). To determine the effect of solution acidity on the efficiency of adsorption, pH of the solutions was adjusted between 1-10 for Cr (VI) ions. Adsorption experiments were carried out by keeping other parameters constant.

3.5.5 Effect of Initial Concentration

This step determines the effect of metal ions concentration on metal ions removal efficiency of adsorbent (water hyacinth stems low cost activated carbon). The effect of metal ions concentration will be determined using concentrations of 10, 20, 30, 40, 50 and 60 mg/L for each metal ion and keeping other parameters constant.

3.6 Kinetic Models of Heavy Metal Adsorption on Water Hyacinth

Kinetic models are used to examine the rate of the adsorption process and the potential rate determining step and for this work in order to model the adsorption of Cr(VI) ion onto water hyacinth activated carbon pseudo first and second order kinetics were applied. The linear form of pseudo first and second order equations are expressed in equation and respectively. The kinetic studies were conducted using 100 ml aqueous solutions of Cr(VI) ion concentrations 50 ppm, adsorbent dosage 1.0 g (weighed using Mettler Toledo model XS105) of ground water hyacinth ACs whose particle size was 0.150 mm added in 500 ml beakers.

The pH value of the solutions in the beaker was set as 2.0 using a bench top pH meter model HANNA HI 22091, and were adjusted by adding 0.1M HCl and 0.1 M NaOH. Adsorption was allowed to occur for 2 hours. The mixture was filtered using gravity filtration (using Whatman filter paper no. 40 and plastic filter funnels). The concentrations (C₃) of selected heavy metal ions were determined. The recorded concentrations (C₁ and C₃) were used to determine the adsorption efficiency of water hyacinth ACs (q). The data obtained was used to draw a plot that was used to determine the reaction order which described the adsorption of the heavy metal on water hyacinth bio material. Pseudo-first order and pseudo-second order which were applied are shown in Equations 3.4 and 3.5 respectively.

The linear pseudo-first order equation is;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \text{-----(3.4)}$$

Where q_e and q_t (mg/gm) are the amounts of chromium adsorbed at equilibrium and at time t , respectively and k_1 is the equilibrium constant (min-1). Integration of equation (3.5) and by applying the initial conditions $q_t=0$ at $t=0$ and the linear form can be formulated as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \text{-----(3.5)}$$

The linear pseudo-second order equation is;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \text{-----(3.6)}$$

where q_e (mg/g) amount of heavy metal adsorbed on water hyacinth at equilibrium K_1 (min-1) rate constant of adsorption for pseudo-first order q_t (mg/g) amount of heavy metal adsorbed on water hyacinth ACs at time t K_2 (g mg-1min-1) rate constant of adsorption for pseudo-second order The adsorption rate constant (k_1) for pseudo-first order was computed from the gradient of a linear plot of $\log(q_e - q_t)$ vs t while q_e was the value of the intercept. The adsorption rate constant for pseudo-second order (k_2) and q_e were computed from the gradient and intercept of a linear plot of t/q_t vs t . The linear plot with the highest R^2 value was considered to describe the reaction best and was taken as the correct reaction order.

4. Result and Discussion

4.1 Characterization of Prepared Samples

4.1.1 The FT-IR Spectroscopy

Functional groups in SWH AC was determined using FT-IR spectroscopy (Fig. 4.1 a and b). The WHS is cellulosic materials mainly contains cellulose, hemi-cellulose and lignin. The FT-IR spectra of SWH AC before and after adsorption of Cr (VI) was performed to determine the vibration frequency changes in their functional groups within the range of $4000 - 400 \text{ cm}^{-1}$. The SWH spectrum showed numbers of major intense bands, around 3424, 2371, 1639, 1169, 1007, and 491 cm^{-1} . The broad band around 3424 cm^{-1} is attributed to the existence of free and intermolecular bonded hydroxyl groups. The peaks assigned at 2371 cm^{-1} represented aliphatic C-H stretching vibrations. The band at 1639 cm^{-1} was assigned to the asymmetric stretch mode of the COO^- group. A characteristic band at 1169 cm^{-1} corresponds to the C = C linkages, which is present in the guaiacyl ring of the lignin (Das et al., 2015). The band at 1169 cm^{-1} can be inputed to the CH_2 present in the cellulose and hemi-cellulose (Sun et al., 2008). It was attributed to absorption by C-O stretching in acetyl group in hemicelluloses, the vibrational modes of the $-\text{CH}_2\text{OH}$ groups and the stretching of the IR spectra of the C-O bonds. The bands near 1639 cm^{-1} is due to C=C stretching vibration in aromatic ring and is observed for all samples. The weak band appearing at 1169, 1007 cm^{-1} are due to formation of highly conjugated (C=O stretching, C-O stretching in carboxylic groups and carboxylate moieties). The strong peak band around around 1007 and 491 cm^{-1} show the bending vibrations hydrocarbons on the surface (Cheng J. et al., 2016). The spectra of the water hyacinth powder before and after adsorption of chromium ions are presented in figure 4.1a and 4.1 b respectively.

Figure 4.1: a= Spectra for stem water hyacinth AC before Cr(VI) adsorption and b= spectrum for chromium loaded stem water hyacinth AC.

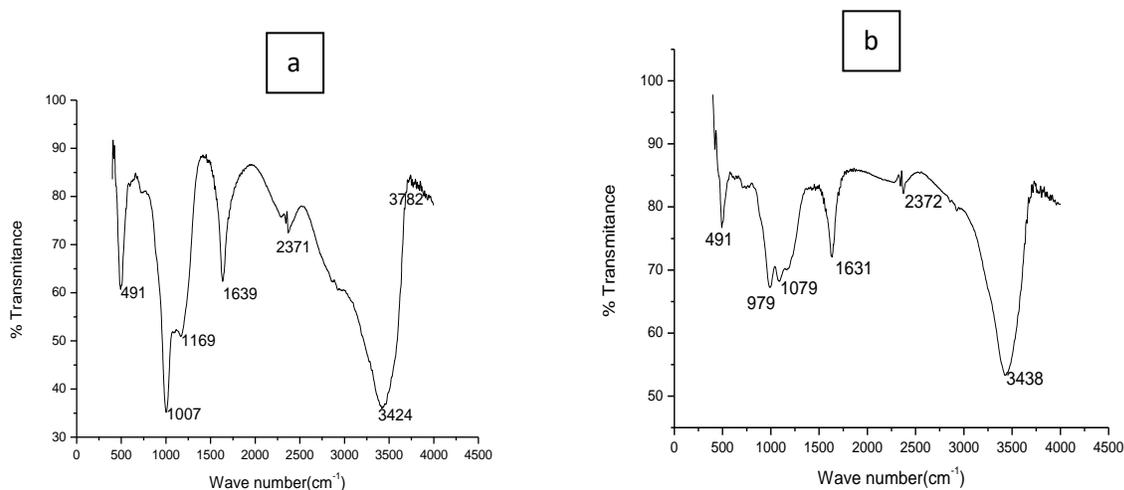


Figure 4. 1 (a) SWH AC before adsorption (b) SWH AC after adsorption

Table 4. 1 FTIR spectrum of SWH AC before and after adsorption

Frequency(cm^{-1}) before adsorption	Frequency(cm^{-1}) after adsorption	Bond	Functional groups
3424	3438	O-H stretching bond	Hydroxyl
2371	2372	C-H stretching bond	Aliphatic
1639	1631	C-O stretching	Carboxyl
1169	1079	C=O bending	Carboxyl
1007	979	C=Cbending vibration	Alkene

4.1.2 XRD Analysis

XRD patterns of the activated carbon with out treated with the chromium(VI) solution is shown in Fig. 4.2 Broad peaks were obtained XRD pattern of the activated carbon without treated with the chromium (VI) solution step scan of 1.05s were used for the entire reading range (0 to 100°) as shown in figure 4.2. There is a peak around 22° reflection which carresponds to the (200) crystallographic plane(Tserki et al., 2005). For materials that have high cellulose content like cotton, flax, or other fibers, one may observe two peaks around 16°, but in cases where the content of amorphous materials such as lignin, hemicelluloses and amorphous cellulose is high, the two peak peaks are smeared and appear as one shoulder. Thus the appearance of the one peak

at 20° in the XRD result meets some developed crystallinity but fitted with amorphous materials. The presented study result shows the presence of high content carbon and this could be result of removal of some amorphous constituents of the stem of WH during activation treatment. Similarly Cordeiro et al., (2011b) reported an increase in crystallinity for sisal fiber after H_3PO_4 treatment. Broad peaks were obtained instead of sharp peaks indicating the sample was poorly crystalline.

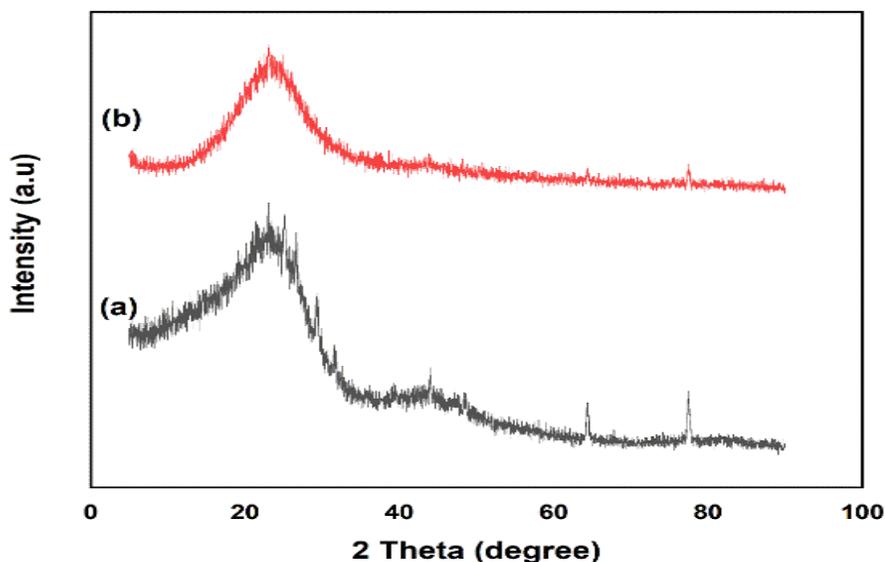


Figure 4. 2 XRD diffractogram of SWH AC

4.2 Effect of Some Experimental Conditions on Cr(VI) Ions Adsorption from Aqueous Solutions

Experimental conditions that affect Cr(VI) ions adsorption from aqueous solutions are the changes of pH solution, time adsorption, adsorbent dose and initial concentration of Cr(VI) ions solution are investigated. Finding the optimum pH, dose and contact time is very important for determining the maximum possible adsorbate removal. For this purpose, 100 ml of test solution of known concentration was added to each conical flask and equilibrated with an adsorbent dose of 1.0 g while varying pH.

4.2.1 Effect of pH Solution

pH is an important factor that controls the adsorption process. When changing the pH of solutions and fixing other factors (the initial Cr(VI) ions concentration of 30 ppm, the adsorption time of 60 min, and the adsorbent weight of 0.2 grams). The effect of pH on removal of Cr(VI) was studied at pH 2.0 to 10.0. The highest percentage removal efficiency was found at pH 2 as shown in figure 4.3. Removal efficiency decreases from 93.4% to 69 % as pH increases from 2.0 to 10.0. Thus, high adsorption of Cr(VI) was observed at low pH and the removal decreased with increase in pH (Mohammad, 2012). Eichhornia contains many functional groups. The variation in adsorption may be due to the type and ionic state of these functional groups and metal chemistry in solution (Matheicksl et al. 1999). At acidic pH, the predominant species of Cr(VI) were $\text{Cr}_2\text{O}_7^{2-}$, HCr_2O_7 and CrO_4^{2-} . The Cr (VI) ions are in form of acidic chromate ions (HCr_2O_7) and CrO_4^{2-} . When the pH of solutions increases from 6 to 7, the Cr(VI) ions will be changed in to Cr_2O_7^- and CrO_4^{2-} . In pH 7 solution Cr (VI) ions are only in CrO_4^{2-} form and in solution pH higher 7, Cr (VI) ions will be in the form of $\text{Cr}(\text{OH})_6$.

The hexavalent species exist primarily as chromic acid (H_2CrO_4) and its salts depending on the pH. The predominant species present, as a function of pH are H_2CrO_4 at pH less than or about 1, HCrO_4^- at pH between 1 and 6 and CrO_4^{2-} at pH 6 or above. It can be said that the removal of Cr(VI) at low pH is due to the electrostatic attraction of positively charged surface functional groups with species. At low pH the functional group carries positive charge and as the pH increases the adsorbent surface possesses more functional group carrying a net negative charge which tends to repulse the anions (Gupta et al, 2001).

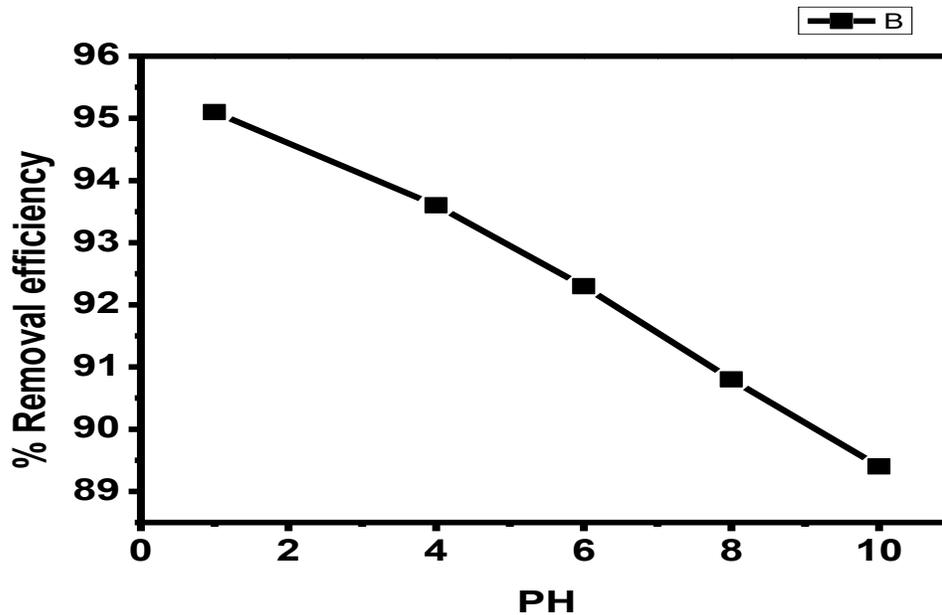


Figure 4. 3 ; Effect of pH on removal efficiency of Cr(VI) ion from aqueous solution using water hyacinth activated carbon at : $C_0=30$ ppm , $t= 60$ minutes and adsorbate dose= 1.0 gram

4.2.2 Effect of Adsorption Time

Contact time is an important factor in the process of evaluation of the adsorbent. The batch experiments were carried out at different contact times 10-160 min. Adsorption time influences strongly the Cr (VI) ions adsorption ability of low cost water hyacinth activated carbon sample as fixing other adsorption factors (the initial Cr(VI) ions concentration of 30 ppm, the pH of 2, and the adsorbent weight of 0.2 grams). At the beginning, the ions adsorbed, occupied the active sites on the phases. It can be seen that adsorption of Cr(VI) ions are increased as rising adsorption time. This result indicates that the adsorption of Cr(VI) ions onto low cost activated of WHS sample requires a long stirring time. However, the adsorption ability were augmented extremely at the adsorption time of 60 min, and they were then varied slowly. The adsorbent with many active sites adsorbed a large part of Cr(VI) ions in the solution for first 60 min. While adsorption time is over 60 min, the occupation of these adsorption sites by Cr(VI) ions causes the reduction of the availability of active sites in the adsorbent sample. On the other hand, there is a possibility of release back of Cr(VI) ions from the surface of adsorbent sample to solution due to

the weak interaction between the adsorbent and the ion target. Therefore, the period of 60 min was considered to reach adsorption equilibrium or equilibrium time.

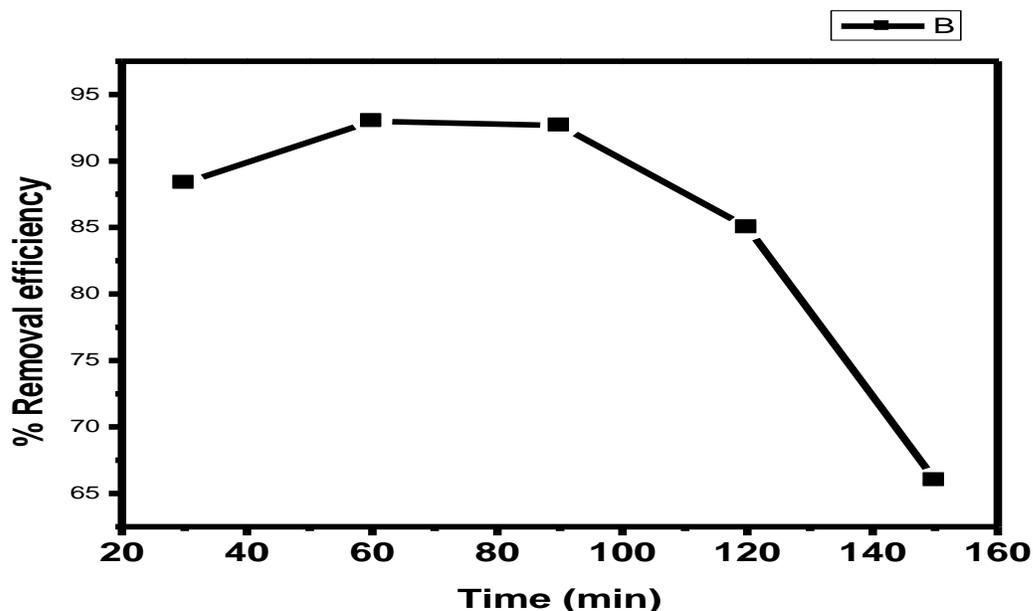


Figure 4. 4: Effect of contact time on removal efficiency of Cr(VI) ion from aqueous solution using water hyacinth activated carbon at : pH =2, adsorbent dose=0.2 gram and Co = 30 ppm

4.2.3 Effect of Adsorbent Dosage

The mass adsorbent of SWH was varied from 0.5_2.5 g and fixing all the other experimental variables constant (the initial Cr(VI) ions concentration of 10 ppm, the pH of 2 and the time contact of 60 min). In this study it was found that on increasing the adsorbent weight adsorption of Cr(VI) gradually increases percentage removal of Cr(VI) ion from 93.4% to 94.26% this may be due to the increase in availability of surface active sites resulting from the increased dose of the adsorbent, then decreased to 53.4% at 2.5 gram weight of adsorbent. The Cr(VI) ions adsorption ability of low cost activated carbon of WHS sample was increased because the higher volume of materials, the more voids to increase the adsorption ability of Cr(VI) ions into the adsorption material. The Cr(VI) adsorption on SWH low cost adsorbent increases with increase in adsorbent

weight until 1.0 g, since contact surface of adsorbent particles increased and it would be more probable for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions to be adsorbed on adsorption sites. After 1.0 g, the adsorption was decreased such behavior is expected due to saturation level attained during adsorption process (Dubey and Gopal, 2007).

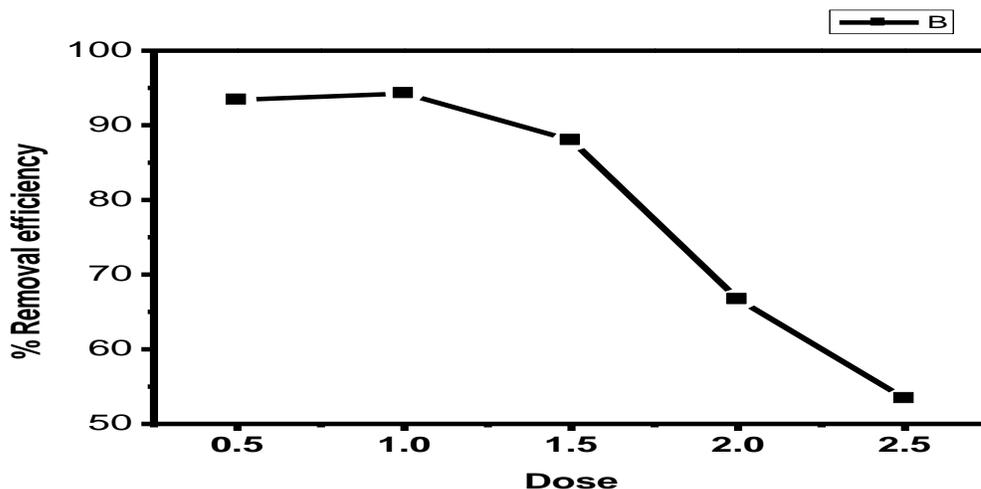


Figure 4. 5 ; Effect of adsorbent dose on removal efficiency of Cr(VI) ion from aqueous solution using water hyacinth activated carbon at : pH =2 , t= 60 minutes and Co = 30 ppm

4.2.4 Effect of Initial Cr(VI) Ions Concentration

Effect of initial Cr(VI) Ions Concentration on percentage removal was studied as shown in figure 4.6. The effect of initial concentration on the Cr(VI) ions adsorption ability of WHS adsorbent sample is carried out at condition of pH 2 with adsorption time of 60 min and the adsorbent dosage of 1.0 gram. The percentage removal of the Cr(VI) Ions was found to decrease from 90.26% to 53.25%. The effect of initial Cr(VI) Ions Concentration relies on immediate relation between the Cr(VI) ions concentration and available binding sites on the adsorbent surface. The removal efficiency will decrease an increase initial Cr(VI) concentration due to the unsaturation of adsorption sites on the adsorbent surface (Eren and Ascar, 2006). There will be unoccupied binding sites on the adsorbent surface at a low Cr(VI) ion concentration and when the initial Cr(VI) ion concentration increases, there will be insufficient sites for the adsorption of Cr(VI) ions, thus decreasing the Cr(VI) ion removal efficiency (Salleh et al., 2011).

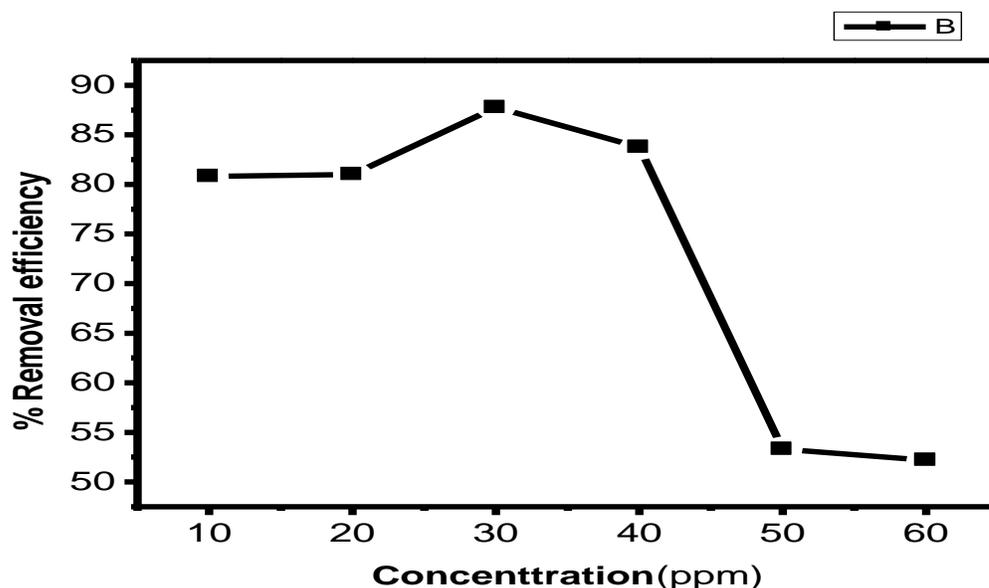


Figure 4. 6 ; Effect of initial concentration on removal efficiency of Cr(VI) ion from aqueous solution using water hyacinth activated carbon at : pH = 2, t= 60 minutes and adsorbate dose= 1.0 gram

Table 4. 2 Comparison of adsorption % Cr (VI) ion onto water hyacinth and other different adsorbents found in literatures.

Name of adsorbent	% Removal of Cr (VI)	Adsorbent Dose	Reference
Alfa Grass(<i>StipaTenacissima</i>)	92.36	3.8 g/L	Tazirout and Amarani,2009
Neem leaves	85	8 gm/L	Pandhran and Nimbalkar,2013
Potato peels	96	4 g/L	Mutungo et al., 2014
Trapa natans husk	99	1.5 g/L	Liu et al., 2010
Olive stones	87	0.25 g/L	Attia et al., 2010
Acid Treated banana peel	99.53	0.2 g/L	Kumar and Majumder,2014
Modified orange peel	41.4	4 g/L	Mandina et al., 2013
Crude tamarind	99.09	4.6 g/L	Sudhanva et al., 2014
Bamboo(<i>Oxytenanthera abssinica</i>)	98.28	0.015 g/L	Hiranmai Yadav, 2014
Raaw rice husk	66	70 g/L	Nasim et al., 2004
Activated bagasse carbon	99.97	0.8 g/L	Nasim et al., 2004
SWH Activated Carbon	94.26	1.0 g/100 mL	Present study

4.3 Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate as a function of its concentration at constant pressure. Adsorption isotherm is important to describe how adsorbate interact with adsorbents and so it is important in optimizing the use of adsorbents. Two common isotherm equation namely, Langmuir and Freundlich models were tested (Demiral H, 2008).

4.3.1 The Langmuir Isotherm

Assumes a surface with homogeneous binding sites equivalent sorption energies, and no interaction between adsorbed species. Its mathematical form is written as:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \text{-----4.1}$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the chromium (mg/L), constant b is related to the energy adsorption (L/mg), Q is the Langmuir monolayer adsorption capacity (mg/g). The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L .

$$R_L = \frac{1}{1 + bC_0} \text{----- (4.2)}$$

Where, C_0 is the highest initial concentration of Cr (VI) ions (mg /L)

b is Langmuir adsorption constant obtained from slope of Langmuir plot(L/mg).

R_L indicates the type of isotherm to be reversible ($R_L=0$), favorable($0<R_L<1$), Linear ($R_L=1$) or unfavorable ($R_L>1$)(Pavan FA, 2008).

4.3.2 The Freundlich Isotherm

The Freundlich Isotherm model is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \text{-----(4.3)}$$

Where q_e is the amount adsorbed at equilibrium (mg/g)

k_f is constant that describes roughly indicator of adsorption capacity of the adsorbent (mg /g)

n is empirical parameter that dictates the intensity of the adsorption.

$1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption

C_e is the equilibrium concentration of chromium (mg/L). The values of k_f and n can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$ of the Freundlich Plots. A linear plot of $\ln q_e$ versus $\ln C_e$ confirms the validity of the Freundlich model.

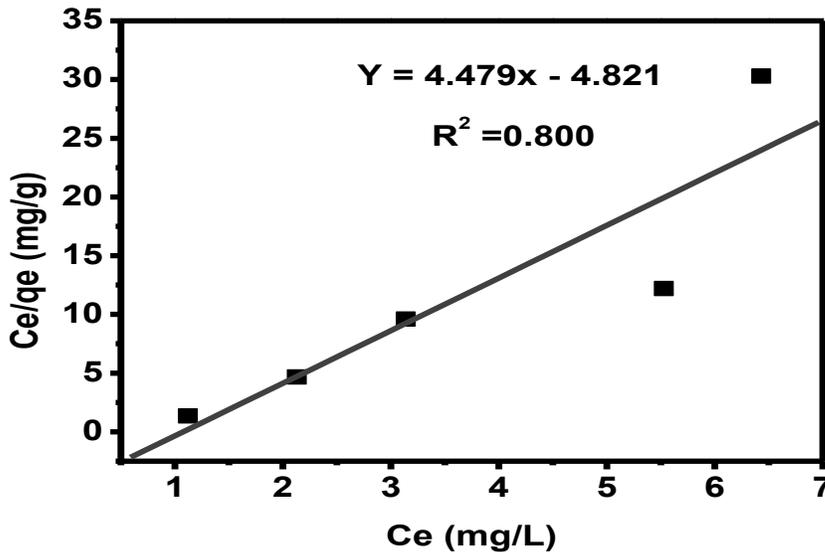


Figure 4. 7 Linearized Langmuir plot for the adsorption the adsorption of Cr(VI) ions onto SWH AC

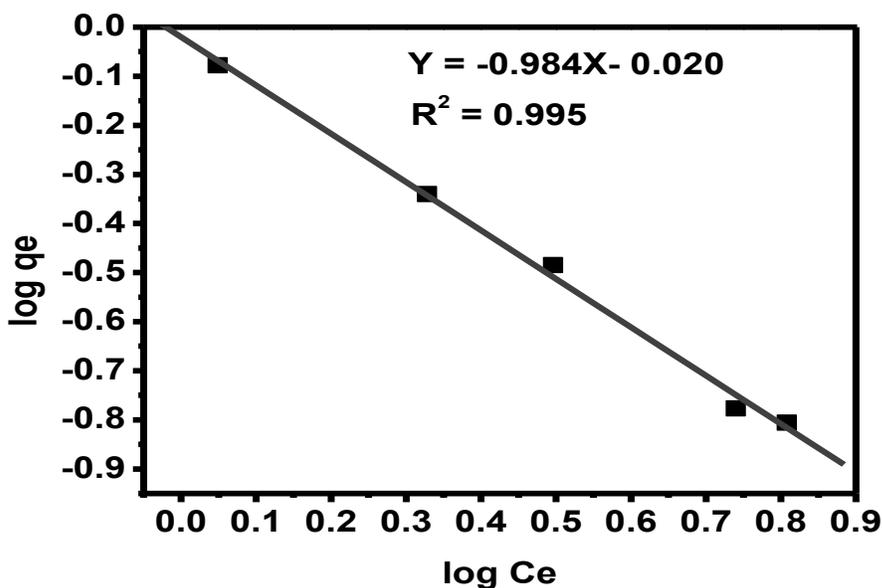


Figure 4. 8 Linearized Freundlich plot for the adsorption the adsorption of Cr(VI) ions onto SWH AC

Figure 4.7 and 4.8 show the linear plot of Langmuir and Freundlich isotherms for adsorption of Langmuir of Cr(VI) ion on SWH activated carbon.

Table 4. 3 Parameters for Langmuir and Freundlich isotherms for adsorption of chromium ions on SWH activated carbon

Langmuir		Freundlich	
b=4.821	N= 1/b=1/4.479=0.22	b=0.020	qm=1.01626
m=4.479	Kf=antilog b= 1.6503	m=0.948	
R ² =0.800		R ² =0.995	

The model parameters obtained by applying Langmuir and Freundlich models to be the experimental data are given in table 4.3. It can be found that the regression coefficients R² obtained from Freundlich model are closer to 1 than that of the Langmuir model, suggesting that the Freundlich isotherm fits better with the adsorption of Cr(VI) ion on SWH activated carbon.

4.4 Adsorption Kinetics

The data obtained from this study were tested against the pseudo-first and pseudo-second order kinetics model. The pseudo-first order equation and the pseudo-second order equation: In order to investigate the controlling mechanism of adsorption process of Cr(VI) ion by SWH activated carbon. The pseudo-first order and pseudo-second order kinetic models were cited to evaluate the experimental data. The pseudo-first order kinetic model has been widely used to predict metal adsorption kinetics. It was suggested for the adsorption of solid/ liquid systems. The differential form of the pseudo-first order model of adsorption can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \text{-----(4.4)}$$

Where q_e and q_t (mg/gm) are the amounts of chromium adsorbed at equilibrium and at time t , respectively and k_1 is the equilibrium constant (min^{-1}). Integration of equation (4.4) and by applying the initial conditions $q_t=0$ at $t=0$ and the linear form can be formulated as(4.5).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \text{-----(4.5)}$$

Where q_e is the adsorption uptake of Cr(VI) ion at time t (mg/g) and k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption. A plot of $\log(q_e - q_t)$ versus t should be linear, the parameters k_1 and R^2 (correlation coefficient) calculated from the data. (Figure 10) are listed in table 5. It can be seen that the linear correlation coefficient (R^2) for the pseudo-first order model are high. However, there are large differences between the experimental q_e values ($q_{e,\text{exp}}$) and the calculated q_e values ($q_{e,\text{cal}}$), which indicated the pseudo-first order kinetic model was poor fit for the adsorption process of SWH activated carbon for Cr(VI). The differential form of the pseudo-second order reaction equation may be written as (Nugulu et al., 2009):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \text{----- (4.6)}$$

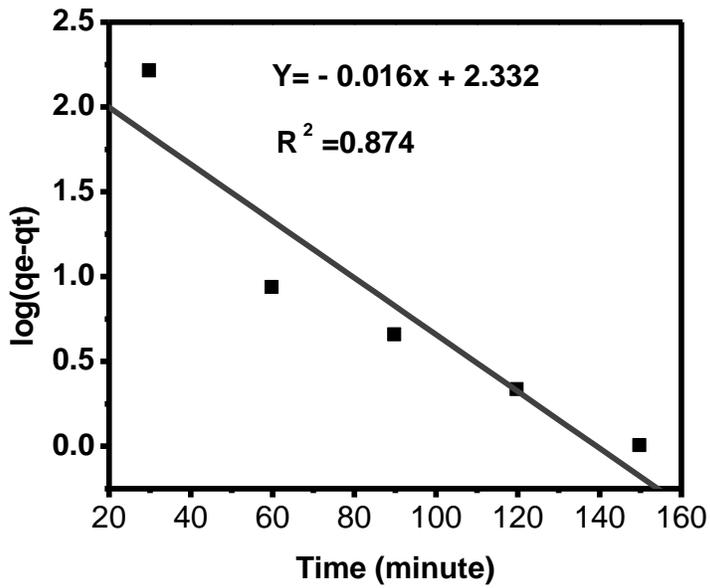


Figure 4. 9 Pseudo first order kinetics for the adsorption of Cr(VI) ion on WHAC

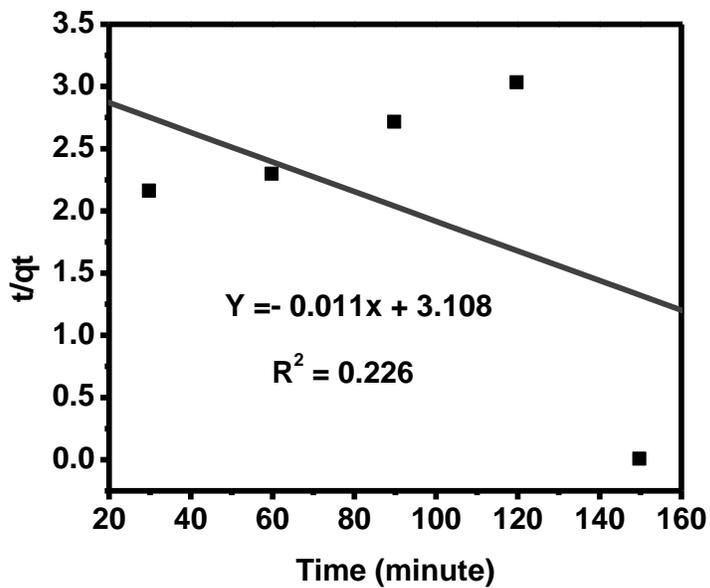


Figure 4. 10 : Pseudo second order kinetics for the adsorption of Cr(VI)ion on WHAC

As it was observed from figure 4.9 and 4.10 that R^2 values for the pseudo-first order kinetic model are over 0.874, moreover, the $q_{e, cal}$ values for the pseudo-second order kinetic model are consistent with the $q_{e, exp}$ values. These suggested that the adsorption processes of SWH activated carbon for Cr(VI) can be well described by the pseudo-second order kinetic model. As observed that the R^2 value for pseudo-first order (0.874) in the adsorption of Cr(VI) ions were higher than that of pseudo-second order (0.226) for the chromium ion. This suggested that the adsorption kinetics of Cr(VI) ions on SWH AC is better expressed by pseudo first order model.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In this study, activated carbon was prepared from water hyacinth stem of lake Awash and used as adsorbing agent for the removal of Cr(VI) ion from aqueous solution in a batch adsorption experiment. The prepared activated carbon was tested using FTIR which showed the active site has acidic functional group. This showed that the surface of water hyacinth stem composed of several different functional groups which include aliphatic groups, carboxylates, aromatic and alcoholic moieties. XRD result indicated there was crystallinity development but synthesis SWH AC was amorphous and highly carbonated. The adsorption experiments were conducted through various parameters such as pH of solution, initial concentrations of Cr(VI) ions, adsorbent dose, and contact time. The maximum percentage removal of Cr(VI) was obtained at pH of 2, contact time 60 minutes, initial Cr(VI) ion concentration of 30 mg/L, adsorbent dose of 1.0 gram, which is 95.5%. The adsorption isotherm model was fitted with Freundlich isotherm model ($R^2=0.995$) than Langmuir isotherm model ($R^2=0.800$). The data obtained were also fitted into pseudo first order and pseudo second order kinetic models and it was observed better that the pseudo first order models provide better fit for the adsorption data. Based on the result of this study, SWH activated carbon is an alternative, inexpensive adsorbent, efficient in the removal of Cr(VI) ion from aqueous solution.

5.2 Recommendation

In this thesis work, the activated carbon was prepared from water hyacinth stem but further study needed to produce the activated carbon from its root and leaf. In order to make the study more comprehensive, it is better to prepare activated at more different temperatures and carbonization time. The adsorption of stem water hyacinth activated carbon must be applied for the removal of other heavy metals and dyes from different industry waste products. The spread of water hyacinth in lake Awash increased from time to time, therefore, it is now recommended that the government should encourage this kind of research work by recommending it to the users of the activated carbon since it has the potential to be adopted in industrial scale.

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