2022-07

Removal of Hexavalent Chromium and Methylene Blue from Tannery & Textile Wastewater by Adsorption Using Carbon Derived from Water Hyacinth Leaf

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http://ir.bdu.edu.et/handle/123456789/14007

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A Thesis Submitted to The Postgraduate Program of Bahir Dar University in Partial Fulfillment for The Degree of Master of Science in Industrial Quality Control and Management

July,2022
Bahir Dar, Ethiopia

Declaration

This is to certify that the thesis entitled **"Removal of Hexavalent Chromium and Methylene Blue from Tannery & Textile Wastewater by Adsorption Using Carbon Derived from Water Hyacinth Leaf"**, submitted in partial fulfillment of the requirements for the degree of master of science in quality control & management, department of industrial chemistry Bahir Dar University, is a record of original work carried out by me and has never been submitted to this or any other institution to get any other degree or certificates. The assistance and help I received during this investigation have been duly acknowledged.

Ayenachew Kebad ____________________ _________________________

(Name of the candidate) (Date) (Place)

BAHIR DAR UNIVERSITY
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DEPARTMENT OF INDUSTRIAL CHEMISTRY

Approval of Thesis for Defense

I hereby certify that I have supervised, read, and evaluated this thesis titled **“Removal of Hexavalent Chromium and Methylene Blue from Tannery & Textile Wastewater by Adsorption Using Carbon Derived from Water Hyacinth Leaf”** by Ayenachew Kebad prepared under my guidance. I recommend the thesis be submitted for oral defense.

Supervisor’s name	Signature	Date
Department Head	Signature	Date

BAHIR DAR UNIVERSITY

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DEPARTMENT OF INDUSTRIAL CHEMISTRY

Approval of Thesis for Defense Result

As members of the board of examiners, we examined this thesis entitled **“Removal of Hexavalent Chromium and Methylene Blue from Tannery & Textile Wastewater by Adsorption Using Carbon Derived from Water Hyacinth Leaf”** by Ayenachew Kebad. We hereby certify that the thesis is accepted for fulfilling the requirements for the award of the degree of Master of Science in Industrial Quality Control and Management.

Board of Examiners

External examiner name	Signature	Date
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Internal examiner name	Signature	Date
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Chair person’s name	Signature	Date
______________________	_______________	______________

Dedication

This work is dedicated to the Almighty/ Princess of God and his mother St. Marry as well as my family.

Acknowledgment

First and foremost, I would like to thank the Almighty God for giving me health, patience, strength, and calm throughout the entire situation and challenge that I faced for the successful completion of this thesis. And also thank you to wollo University for giving me an opportunity to learn industrial chemistry and to do this thesis, as well as bahirdar University.

I am extremely thankful to my advisor, Maru Dessie (Ph.D.) for his arranging facilities, timely valuable discussion, constructive comments and suggestions and encouragement throughout my study. Without his professional assistance and guidance, this study would not be realized. Besides my advisor thanks to; Fentahun Aklog (Ph.D.), Tesfaye Tollosa (Ph.D.) & Tamene Simachew (Ph.D.) for giving a comment starting from a seminar course up to the thesis work.

I would like to thank you to all MSc industrial chemistry graduates for their encouragement, insightful ideas on how to do /write the thesis paper and best advice in general.

I would like to express my gratitude to Zinabu Gashaw (Ph.D. candidate) for his invaluable and helpful advice, assistance and guidance in using the laboratory equipment which was really useful to my research and greatly enhanced my laboratory works.

I am also thanks to my wife Kalkidan Mihretu. She carried out all family responsibilities and gave me a chance to focus on my study. Finally, I acknowledge all members of my family, relatives, and friends for all their encouragement and support throughout my study.

Table of Contents

Contents Pages

List of Tables

Tables **pages**

List of Figures

Figures **pages**

List of Tables in Appendix

Tables **pages**

List of Abbreviation

ACDWHL	Activated Carbon Derived from Water Hyacinth Leaf
ATWW	After Treatment of Wastewater
ATWWA	After Treatment of Wastewater Adsorption
BTWW	Before Treatment of Wastewater
BTWWA	Before Treatment of Wastewater Adsorption
BET	Brunauer Emmett and Teller
DP	Pore Dimeters
FTIR	Fourier Transform Infrared Spectroscopy
MB	Methylene Blue
MF	Microfiltration
NF	Nanofiltration
PHPZC	Point of Zero Charge
TWW	Tannery Wastewater
TXWW	Textile Wastewater
TS	Types of Samples
UV	UV–Vis-Spectrophotometer
WHO	World Health Organization
XRD	X-Ray Diffraction

Abstract

Chromium (Cr (VI) and methylene blue (MB) released from industry lead to a significant environmental pollution and have a tendency to accumulate in a certain part of the human body and become harmful to life. In this study water hyacinth leaf were used for the preparation of activated carbon to use it as an adsorbent for the removal of chromium (Cr (VI) and methylene blue (MB) from Tannery and Textile wastewater. The water hyacinth was collected from the coastal of Abay River. The waste samples were taken from pre-treatment & post-treatment sites outlet of leather & textile industry from Bahir Dar leather & textile production which are found in Bahir Dar City, Ethiopia. The activated carbon derived from the water hyacinth leaf (ACDWHL) were characterized through proximate analysis, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) & Brunauer Emmett and Teller (BET) analysis. The batch adsorption experiments were conducted by varying pH:1–8 & 6-14, dosage:50-250 mg/50ml, initial concentration:2–10ppm and contact time: 30-180 min, at room temperature for Cr (VI) and MB respectively. The optimum values are pH = 2 & 10, dose = 150 & 200 mg, concentration = 2 ppm and contact time = 120 & 90 min were obtained for Cr (VI) and MB removal, respectively. After carbonization, the carbon derived material from the water hyacinth leaf shows high- surface area of 616.387 m^2 g^{-1}, pore volume of 0.2064 cm^3 g^{-1} and pore diameter of 0.2261 nm was obtained at 2:1 impregnation ratio with 500°C temperature for 2hr of carbonization time. At the optimized pH the removal efficiency of ACDWHL for Cr (VI) and MB were 84.4 & 95.2%, respectively. In addition, the maximum adsorption capacity of Cr (VI) and MB was determined to be 7.4 and 8.12 mg g^{-1}, respectively. Electrostatic interaction acting a major role during these adsorptions due, to anionic species of Cr (VI) and cationic forms of MB. The conducted adsorption isotherm and the adsorption kinetic studies explained that data fitted well with Langmuir & Freundlich isotherm for Cr (VI) & MB respectively, and correlated well with the pseudo second order. Finally, its concluded that ACDWHL was a satisfactory adsorbent for mitigation of Cr (VI) and MB from tannery & textile industries effluent.

Keywords: - Adsorption; Activated Carbon; Hexavalent Chromium; Methylene Blue;Adsorption Isotherm; Adsorption Kinetics

1 INTRODUCTION

1.1 Background

Water contamination is an issue that affects people (living things) throughout the globe. It can be geological or anthropogenic (man-made) [1]. The naturally occurring elements present at intolerable levels and man-made by-products of industry and agriculture including heavy metals like mercury, copper, chromium, lead and harmful chemicals such as dyes and compounds like insecticides and fertilizers contaminating the water [2].

The tanning industry is a well-known as one of the major water polluting industries which generates a large amount of effluent throughout the tanning process [3]. Various chemicals have been using for the processing of leather including lead, nickel, arsenic, chromium and cadmium. However chrome tanning process is the most frequently used for tanning process [4, 5]. Wastewater produced from tanneries is highly contaminated or polluted with high organic and inorganic pollutants [6].The organic load is due to the existence of hair, manure, soluble protein and blood particles but the inorganic load is mainly due to the existence of the chromium salt which is used as a tanning agent [7].

Chromium [Cr (VI)] is a major toxic heavy metal for both humans and the environment [8]. Chromium enters the environment through wastewater generated by anthropogenic sources, such as steel and alloy manufacture, bricks, chromium plating, metal finishing and textile dyeing [9]. In aquatic environment, chromium exists as both the trivalent [Cr (III)] and hexavalent [Cr (VI)] oxidation states [10]. The trivalent form is less toxic than the hexavalent and is widely known as a supplementary mineral for human health, while [Cr (VI)] is a potential carcinogenic, mutagenic skin irritation and liver damage [8]. The recommended limit to [Cr (VI)] in potable water, inland surface water and industrial wastewater was 0.05mg/l on the bases of world health organization (WHO) [11, 12].

Correspondingly, methylene blue (MB) is a cationic dye, which is discharged by paper and pulp, textile, leather, plastics and food industries [13]. The methylene blue exposure leads to human health effects such as ; shock ,vomiting, eye burns and irritation to the skin [14].

Consequently; it is necessary to treat industrial wastewater incorporate chromium and methylene blue before being discharged to the environment. The common strategies that have been employed to remove Cr (VI) and MB from the tannery and textile sewage are ion exchange [15, 16] ,chemical precipitation [17], flotation [18], membrane filtration [19] and adsorption [5, 20]. In comparison with these methods, adsorption is one of the efficient and multifaceted mechanism that has been used to remove chromium and methylene blue from wastewater comparatively at low adsorbent amount. This is due to its simplicity, cost-effectiveness, non-hazardous technique, easy operation and almost without secondary sludge production [21, 22].

In recent years, numerous researchers have used many adsorbents such as rice husk carbon [23], treated waste newspaper [24], peels of peapod [25], corncob-based activated carbon[26], bamboo charcoal [27] and clay [28], for the removal of Chromium and methylene blue from wastewater. Moreover, Ajay Kumar Manna and co-workers have been prepared the activated carbon synthesized from natural rubber and employed for the adsorption of Cr (VI) and MB, with the maximum efficiency was 80% [29]. Several investigations have reported that activated carbon has shown a significant adsorption removal efficiency of Cr (VI) and MB [24, 30].

Therefore, to obtain an efficient biomass derived materials for the adsorption of Cr (VI) and MB from the industrial wastewater yet remains a high challenge. Water hyacinth is a noxious weed that has a prompt growth rate and highly reducing the water body, water volume, and aquatic organism. For example, water hyacinth in Abay River, Ethiopia. To acquire and achieve high removal efficiency of Cr (VI) and MB, it is necessary to develop environmentally available biomass derived carbon materials which shows strong adsorption efficiency for both Cr (VI) and MB, that has not been explored and reported yet. The purpose of this thesis work is to develop a low-cost and highly efficient water hyacinth leaf derived activated carbon for the removal of Cr (VI) and MB from tannery and textile wastewater in Bahir Dar City, Ethiopia. The second investigation was to conduct batch system to optimize the effects of adsorbent dosage, solution pH, contact time and concentration using the prepared activated carbon. The obtained activated carbon has been characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET). Adsorption kinetics was assessed by fitting the experimental data with the selected kinetic models.

1.2 Statement of the Problem

One of the major challenges of the present day is the wastewater discharged from industries, particularly in developing countries like Ethiopia. Water is a medium for the metabolic activities of living organisms they need pure water or free from any contaminants [31]. But different natural and anthropogenic contaminants affect the purity of water. Chromium and methylene blue are the common potential pollutants that are often used in industries such as painting, cement, mining, production of steel and other metal alloys, car manufacturing, textile, electroplating, tannery industries, photographic material, corrosive painting and others [9, 13]. The discharges of these effluents into the environment and water bodies cause serious health problems such as skin ulcers, liver disease, kidneys damages and lung cancer [8]. So that ,Cr(VI) and MB potentially affecting the environment, due to their chronical health problem, we need to remove those pollutants [32].

Hence, these pollutants need to treat before they discharged to the environment because of their allergic, dermatitis, skin irritation mutagenic and carcinogenic effects. Even though different reports are available on chromium and methylene blue removal using different natural adsorbents, however, removal of chromium and methylene blue from aqueous solution or wastewater using activated carbon derived from water hyacinth leaf (ACDWHL) has not been yet reported in Ethiopia. The use of water hyacinth leaf as a potential source of activated carbon for the elimination of chromium and methylene blue from the wastewater is an environmentally approachable and practical waste conservation method. This study would provide information on the efficiency of activated carbon derived from water hyacinth leaf towards the removal of chromium & methylene blue in Bahir dar City, Ethiopia from tannery & textile waste /aqueous solution by the adsorption method.

1.3 Objectives of the Study

1.3.1 General Objective

To develop a new and highly efficient biomass derived adsorbent from water hyacinth leaf for the removal of chromium (VI) and methylene blue from wastewater.

1.3.2 Specific Objectives

- To prepare a low cost and environmental-friendly biomass derived activated carbon from water hyacinth leaf, which is utilized as an adsorbent.
- To investigate the influence of pH, concentration, contact time and dose of adsorbent to remove Cr (VI) and MB from wastewater/aqueous solution.
- To characterize activated carbon derived from water hyacinth leaf.
- To investigate the efficiency of activated carbon derived from water hyacinth leaf to remove Cr (VI) and MB from wastewater/aqueous solution.
- To study the kinetics and isotherm models for the adsorption of Cr (VI) and MB into water hyacinth leaf adsorbent.

1.4 Significance of the Study

- Using low-cost adsorbents which could be easily available and environmentally friendly to remove Cr (VI) and MB from industrial wastewater.
- Increase purity of water by removing chromium (VI) and methylene blue.
- Reduce the health problems caused due to high chromium (VI) and MB concentration
- Using natural resources for industrial as raw material input rather than throw away to the environment.
- Reduce environmental waste by using water hyacinth leaf wastes as an adsorbent rather than simply discharging or accumulate into the environment.

1.5 Scope of the Study

The thesis work has been conducted on industrial wastewater obtained from the outlet of the leather and textile industry so-called Bahir Dar leather & textile production which it is found around Bahir Dar City. The scope of this study was to remove Cr (VI) and methylene blue from industrial wastewater using activated carbon derived from the water hyacinth leaf. The characterization of the adsorbent has been caried out using XRD, FTIR, BET and UV-Vis Spectrophotometry.

2 LITERATURE REVIEW

2.1 Wastewater

It is a water whose physical or chemical properties have been changed due to the introduction of certain materials that results unsafe for different purposes such as drinking and which is generated from homes, private institutions, rural areas, urban areas, farms, industries and other point and non-point sources [33]. High amounts of liquid waste from agricultural, industrial, domestic and commercial bases are discharged into raw surface water bodies every day [34]. Industrial wastewater consists of harmful suspended and dissolved substances like heavy metals and dyes that pollute water which, outcomes harmful health problems to living organisms. According to available evidence, including the world health organization heavy metals are urgent environmental concern, including lead, chromium, mercury, cadmium, copper and iron [35].

The development of industrialization most developing countries like, ethiopia has attracted foreign investments but has led to heavy pollution of water bodies due to the discharge of untreated industrial waste. This pollution has been great concern to governments and other stakeholders; therefore, exploring low-cost and effective treatment techniques is the focus of many researchers and scientists across the world [36].

2.2 Heavy Metals

Although there is no specific definition of heavy metals, the literature defines it as a naturally occurring element with a high atomic weight and a density of five times that of a water or any metallic chemical element that has a relatively high density and toxic or poisonous at low concentrations [37]. Among all the pollutants, heavy metals have received paramount attention from environmental chemists due to their poisonous nature and they are commonly found in trace amounts in natural waters but many of them are dangerous even at very low concertation [38]. Metals such as arsenic, lead, cadmium, nickel, mercury, chromium and cobalt are all highly poisonous metals even in trace amounts [39]. They may pass into the human body through food, water, air or absorption through the skin when they come in contact with humans in agriculture, manufacturing, pharmaceutical and industry [36, 38].

2.2.1 Health Effects of Heavy Metals

The gradual accumulation of toxic chemicals in the body of a living organism can results in bioaccumulation, which was produced when an organism uptakes a toxic substance at a higher concentration than its release [34]. As these elements cannot biodegrade or break down easily the negative effects are degenerated by the ecosystem of the environment [40]. For example, Cd can be accumulated in the human body for up to 30 years, without being destroyed /biodegrade or break down [41]. Heavy metals express their toxicity to human beings, which may result from the following mechanisms [42]. Firstly, heavy metals can easily form precipitates with anionic substances (CO_3^{-2}, SO_4^2 and PO_4^{-3}), the precipitates (solids) may stay in the human body. Secondly heavy metals can be adsorbed onto organic functional groups in various tissues of the human body, which may change their biological activities (e.g enzymes),this may also force the essential metals to detach from enzymes and be replaced by harmful heavy metals (e.g, Cu versus Zn).Thirdly some heavy metals may cause redox reactions forcing the basic elements like carbon to change their chemistry for example, hexavalent chromium (CrO_4^{-2}) can cause the oxidation of carbon in the tissues of the human body & the carbon may be oxidized , thus its chemistry may be changed [43]

Therefore, the need to treat wastewater is a great importance to safeguard the environment and reduce associated health problems [44]. It is important to eliminate heavy metals and MB b/c living organisms are easily exposed to different diseases such as carcinogens, mental disorders, kidney damage, lung disease, liver disease, high blood pressure, headaches and intestinal problems [34].

2.2.2 Chromium

The name is derived from the Greek word chroma which means color because many of its compounds are colored [45]. It is an odorless and tasteless metallic transition element with an atomic number of 24, atomic weight of 51.996 and belongs to in the group VI-B of the periodic table with a ground-state electronic configuration of $[Ar]$ $3d^5 4s^1$ [46, 47]. It comes in different natural isotopes namely ^{52}Cr (83.8%) & ^{53}Cr (9.65%) [48] .

Chromium can exist in nine different oxidation states from -II to +VI but the most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI) species. Compounds with a chromium oxidation state of III was strongly reducing state while chromium (VI) compounds are strongly oxidizing states [47, 49].

The majority of chromium (VI) compounds are highly soluble, whereas most of the chromium (III) compounds partially soluble in water. Hexavalent chromium generally exists in monomeric ($HCrO_4^-$ & CrO_4^{2-}) or dimetric state ($Cr_2O_7^{-2}$) due to the presence of dimeric and monomeric species impacts the orange and yellow colors of solution was produced respectively [50]. Depending on the pH the predominant species present, as a function of pH are H_2CrO_4 at pH less than about 1, $HCrO_4^-$ at pH between 1 and 6, and CrO_4^{2-}at pH above 6 [51].

2.2.3 Uses of Chromium

The metallurgical industries use chromium for the production of stainless steel and nonferrous alloys plating steel. For example, on cars and bicycles, aircraft, silver finish & resistant to corrosion [52]. Chromium in the form of Cr (VI) and Cr (III), used for chrome plating, dyes and pigments like; green, yellow, red & orange colors, textile manufacturing, leather tanning and wood preserving [9]. Cr (III) is an essential element for humans to have normal glucose, protein, and fat metabolism [47, 49].

2.2.4 Chromium Toxicity

It is toxic to humans/animals because it is a strong oxidizing agent and has the potential to be carcinogenic, mutagenic/corrosive. From the two most common oxidation states, hexavalent chromium is more toxic [8, 53] and the mobility is higher than trivalent chromium in the aqueous medium [54]. Another environmentally significant chromium species is the trivalent chromium (Cr(III)) which is considered non-toxic at minute concentrations; however, at high concentrations it can be toxic [21].When Chromium is collected at high levels it causes cancer in the digestive tract, epigastric pain, vomiting, severe diarrhea, hemorrhage, leukemia and bladder cancer [55]. Chromium (VI) in the forms of dichromate ($Cr_2O_7^{2-}$), chromate (CrO_4^{2-}) and CrO_3 are considered as the most dangerous forms of chromium because they having high oxidizing potential, high solubility and mobility across the membranes in living organisms and the environment [8]. Chromium (III)is less toxic as it is fairly insoluble in water mainly bound to the organic matter in soil and aquatic environment and presents lower mobility [49].

2.3 Dye

Dyes have been used as color agents in textile, leather, paper, plastic, rubber, painting, cosmetic, food and pharmaceutical industries & most naturally occurring dyes are obtained from plants and minerals [13]. Natural dyes are unable to satisfy industrial demand because of the huge increase in industrial activity that followed the start of the industrial revolution. W. H. Perkin created the first synthetic dye, aniline purple in 1856, since then, synthetic dyes have increased significantly. Synthetic dyes can be categorized as cationic dyes, anionic dyes and non-ionic dyes (based on the particle charge of the dye) [56]. Because of positive ions are present in the structure of the molecule, cationic dyes are sometimes referred to as basic dyes [56]. Anionic dyes contain acidic, dyes (having negative ions present in their aqueous solution) [57].

Synthetic dyes can absorb light in the visible spectrum (400-700 nm) and they are highly visible in water even at very low concentration [58]. Effluents resulted from industrial activities are generally not suitable for the environment/water body due, to their synthetic origin, high solubility and complex molecular structures [58]. In general, basic dyes, acid dyes, reactive dyes and sulfur dyes are employed in the textile industry [59]. High color, organic content and hazard are all characteristics of dye-bearing effluents from various industries [60]. According to reports, there are more than 100,000 dyes available commercially, and more than $7x10^5$ tones are produced annually [61]. It is also estimated that the total dye consumption in the textile industry worldwide is more than 10,000 tons per year and almost 10–25% of these dyes are discharged as effluents into water sources [62].

2.3.1 Methylene Blue Dye

It is a monovalent cationic heterocyclic aromatic chemical compound with the molecular formula($C_{16}H_{18}N_3SCl$) and chemical name [3,7-bis (Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride] [63]. MB is a basic aniline(aromatic amine) dye that forms a deep blue color & it is used in coloring paper, dyeing cotton wool and color of paper. The removal of methylene blue from any sewage is most important due to the serious environmental damage that can exist as a result of contact with it, particularly in the case of human beings [64].

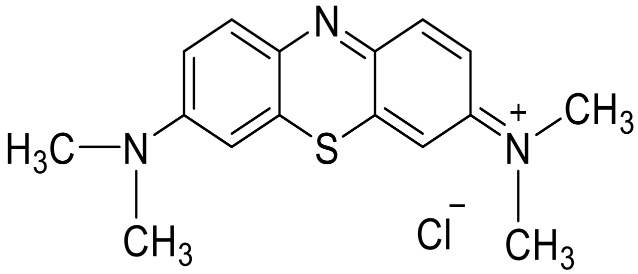

Figure 1:Chemical structure of methylene blue.

2.3.2 Toxicity Effects of Dyes

Since dyes are typically poisonous, discharging them into water sources can have a negative impact on both the environment and human health, since synthetic dyes contain complicated structures so, the public and environmentalists have been concerned about their effects on the environment [65]. Dye discharge into a water body can decrease light penetration through the water and interfere with the photosynthetic activity of aquatic organisms, since dyes are extremely visible in water even at very low concentrations [66]. The textile and paper industries are the major users of cationic dyes like methylene blue and the effluents are the cause of allergic, skin irritation, mutations and even cancer [67]. Also, cationic dyes can cause increased in heart rate, vomiting, decreased cardiac output & blood flow [68].

2.4 Removal Methods of Water Contaminants

Since metals and dyes can exist and accumulate in all living organisms, it is necessary to treat metal and dye-contaminated wastewater before its discharge into the environment [69]. For minimizing these hazardous pollutants various techniques have been employed with varying degrees of success for the removal of toxic pollutants from water and wastewater including chemical precipitation [17], coagulation-flocculation [70], flotation [18], membrane filtration [71], ion exchange resin [72] and adsorption [73].

2.4.1 Chemical Precipitation

It is a simple and widely used approach for removing heavy metals and dyes due to its ease of use and low cost [74]. Chemical precipitation is a technique for treating metal-containing wastewater that involves adding chemicals to generate an insoluble precipitate [75]. Hydroxide precipitation, sulfide precipitation and heavy metal chelating precipitation are some of the several chemical precipitation processes used. Lime and limestones are the most often employed precipitant agents in chemical precipitation [76] . Despite its benefits, it has several drawbacks, such as the use of an excessive amount of chemicals in the treatment process and the generation of excessive sludge and the problem of sludge disposal into the environment [77].

2.4.2 Coagulation/ Flocculation

Introducing a coagulant the coagulation process destabilizes colloidal particles resulting in sedimentation [78] .To raise the particle size, coagulation is followed by the flocculation of the unbalanced particles into large floccules. This technique includes pH adjustment and includes the addition of ferric/alum salts as the coagulant to overcome the repulsive forces among particles. Despite its advantages, coagulation-flocculation has limitations such as high operational costs due to chemical consumption. The improved volume of sludge produced from coagulation-flocculation may difficult its adoption as a worldwide policy for wastewater treatment [79].

2.4.3 Flotation

Employed to separate metal or dyes from a liquid phase using foam attachment and the attached particles are separated from the suspension of metal ions by the bubble rise [80]. Among the different types of flotation, DAF is most frequently used for the treatment of metal-polluted wastewater. DAF allows micro-foam of air to attach to the metal ions in the water & develops with lower density than water and causes the flocs to increase through the water and accumulate at the surface where they can be detached as sludge [81].

2.4.4 Membrane Filtration

Membrane filtration is accomplished by removing suspended solids, organic compounds like dyes and inorganic pollutants such as heavy metals. Depending on the size of the particle that can be retained, several types of membrane filtration such as ultrafiltration & nanofiltration can be employed for heavy metal and dye removal [69].The membrane processes was non-polluting separation methods used in wastewater treatment. In pressure-driven membrane separation processes such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) a pressure gradient over the membrane enables the solvent (water) to permeate the membrane and the solutes existing in the feed solution are rejected to a certain extent, which depends on the membrane type [82].

2.4.5 Ion-Exchange

Ion exchange is a suitable method to remove heavy metal and dyes from the wastewater and this technique has also been applied as a measurement of Cr (VI) and MB [83]. This process uses an interaction or interchanging of ions between the wastewater and solids. For this process metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin [72]. 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 dependent on the pH of water and also including the high cost and selectivity of ions [51].

2.4.6 Adsorption

Mass transfer method by which a material (adsorbate) is moved from the liquid or gas phase to the surface of a solid (adsorbent) and becomes bound by physical or chemical interactions [84]. According to the strength of the interaction adsorbate-adsorbent, it can be divided into physisorption and chemisorption mechanisms. Physisorption (e.g, physical adsorption and micro precipitation) is reacted by weak interactions such as London or Van Der Waals forces, while chemisorption(e.g., ion exchange, electrostatical attraction, coordination & complexation involves the net formation of chemical bonds adsorbent-adsorbate [85].

2.5 Commonly Used Adsorbents

Currently, there are different kinds of adsorbents available for wastewater treatment. Several researchers have used different types of adsorbents to examine their efficiency towards several heavy metals and dyes. From this most commonly used once such as activated carbons, low-cost materials (agricultural waste, natural biomasses, natural mineral materials and industrial by-products) and others [86].

2.5.1 Activated Carbon

It is the most commonly used commercial adsorbent for industrial applications due to its richness in macropores:(>50 nm diameter), mesopores(2-50nm diameter) micropores: (< 2 nm diameter), and the resulting large surface area (500-1500 m^2/g) [87]. Any carbon-containing organic materials can be used to produce activated carbon. Thus commercial activated carbon is manufactured from those that have some original porosity and are easy to activate, such as coal, petroleum coke, wood, sawdust, nutshells, fruit stones, peat & lignite [88].In the effort to reduce costs various kinds of activated carbon have been prepared from agro-byproducts, such as pinewood, rice hull, palm shell, seed husks, coconut shell and palm fruit for sorption [89].

Activated carbon available in different forms like; powdered(a), granular(b) and pellets(c) activated carbon. Powdered activated carbon material is finer material which is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve. Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Correspondingly, as compared from the two activated carbon size pellets is larger , so it has a very smaller external surface area [90].

Figure 2: Activated carbon available in different forms[91].

2.5.2 Low-Cost Adsorbent

Adsorption using low-cost adsorbents has attracted the increasing attention of numerous researchers mainly due to its cost-efficiency, effectiveness, technical flexibility and renewability of used adsorbents [73]. Consumption of naturally occurring materials or industrial by-products or locally existing agricultural waste materials as the adsorbents in removing heavy metals and dyes from wastewaters is not only cost-effective in metal & dye ion removal but also contributes to a zero-waste condition in the environment [69, 73, 92, 93].

2.5.3 Water Hyacinth Leaf (*Eichhornia crassipes)* as an Adsorbent

Water hyacinth (Eichhornia crassipes) is the most quickly growing, very productive free-floating aquatic plant and broadly distributed species that initiated in the amazon & south america [94]. The entrance of water hyacinth into africa, asia, australia and north america was enabled by human activities. Specially, africa has been affected by the entry and distributed of water hyacinth, facilitated in part due to the absence of prevention and removal mechanisms. Water hyacinth reproduces itself very fast by short runner stems and also by seed and it can cover huge water bodies in different countries within a short period [95].

Table 1 Chemical analysis of water hyacinth in different organs[95].

No	Contents	Leaf (%)	Stem (%)	Root (%)
1	Carbon	30.33	29.55	27.22
2	Nitrogen	0.3	0.2	0.1
3	Cellulose	29.86	29.33	18.11
4	Hemicelluloses	31.81	28.35	16.23
5	Lignin	5.49	18.36	15.67
6	Protein	21.97	7.70	3.33
7	Lipid	1.93	0.98	0.65
8	Ash	13.10	21.20	50.11

The contents of cellulose, hemicellulose and lignin in different body part of water hyacinth were mentioned in (table 1). Considering to leaf, stem and root, the whole plant of water hyacinth has a little higher cellulose and hemicelluloses content and low lignin content [95, 96]. Compared the cellulose, hemicellulose and lignin Contents and validity of application, the leaf was finally selected as adsorbent for adsorption of heavy metal and dyes.

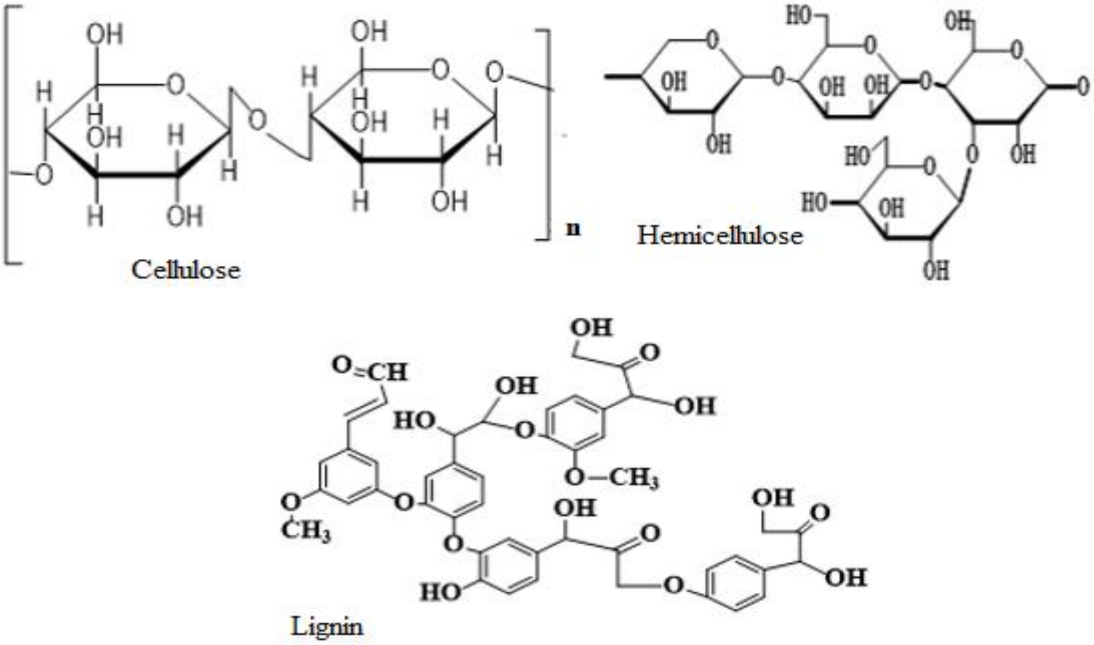

Figure 3: Chemical structure of cellulose, hemicellulose and lignin.

The cellulose, hemicellulose and lignin contains functional groups such as O-H, which are involved in adsorption through hydrogen bond formation & deprotonation [97].Perhaps, this carbon material has earned this title as a result of its characteristics features high surface area, large internal porosity and its availability it could be used in the adsorption of adsorbates.

Abay river, amhara region ethiopia is the one which is covered by water hyacinth as shown in figure 4. Water hyacinth has the ability to reduce water quality, water volume, aquatic organisms and biological variety by blocking photosynthesis, which significantly reduces oxygen levels in the water [98]. Water hyacinth affects biodiversity, ecosystem, human and animal health and socio-economic development significantly. Still now a lot of money and resources are spent including ethiopia in order to avoid the water hyacinth to protect the water body from drying.

Figure 4: Photographic representation of water hyacinth in Abay River.

2.5.3.1 Uses of Water Hyacinth Leaf

Leaf of water hyacinth containing of a high content of cellulose, hemicellulose and proteins which can be used for different application, including; wastewater treatment, bio-fuel production, compost/fertilizer and animal feeds [99].In addition to this the biomass has been used as the adsorbent to remove heavy metals, dyes and for pharmaceutical industries due to its high cellulose and proteins content [100]. Different literatures indicate that water hyacinth has the ability to clean up various contaminated water specially toxic heavy metals and dyes [101].

2.6 Methods to Activate the Carbon

Activated carbon could be prepared through the direct activation of dry fresh precursor or a two-stage process containing initial carbonization and then activation [102]. In the two-stage process, the dried fresh organic materials should be primarily carbonized at high temperatures. In the carbonization process, the material should be exposed to a red spot (less than 700 °C) temperature in the distillation device to evaporate and eliminate the hydrocarbons from it in the absence of oxygen [102]. Generally, the process of carbonization is thus pyrolytic and its product is known as carbonized solid material [103].

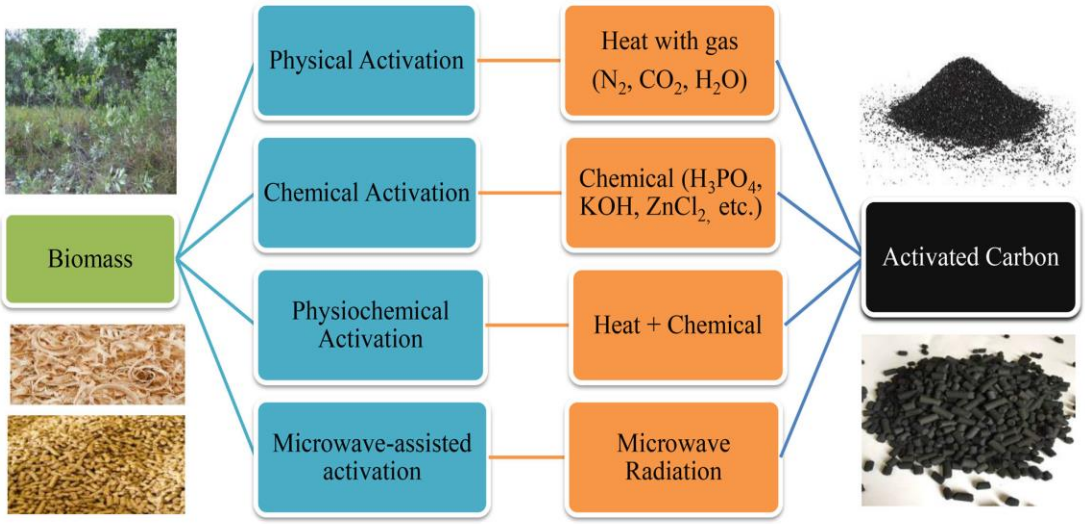

Figure 5: Methods of the activation processes [104].

2.6.1 Physical Activation

Physical activation is a two-step process that begins with carbonization (pyrolysis) in a neutral atmosphere and continues with activation in atmospheric oxidizing gases such as steam, carbon dioxide and nitrogen or air mixtures at temperatures ranging from 800 to 1100°C [102] . This method can produce activated carbon with a porous structure and high physical power and it is a cost-effective method for preparing activated carbon that is also environmentally friendly because it is chemical-free [105] .The long activation time and low adsorption capacity, as well as the high energy consumption are the drawbacks of the physical activation [106].

2.6.2 Chemical Activation

Chemical activation of AC includes both carbonization and activation being accomplished in a single phase using chemical agents [106]. Depending on the activating material and the properties of the last product activation can take place at a temperature variation from 400 to 900 °C at which the material is degraded. These activating agents with in the carbon structure lead to the creation of small pores in the activated carbon, thereby increasing its surface area [107]. Compared to physical activation, this type is more cost-effective since it requires a lower activation temperature, shorter processing time, more porous & higher carbon result [108].

The main chemicals which have been used as a potential activator are alkaline groups such as potassium hydroxide(KOH),sodium hydroxide (NaOH), calcium chloride ($CaCl_2$) & potassium carbonate (K_2CO_3), acidic groups such as phosphoric acid (H_3PO_4) and sulfuric acid(H_2SO_4), as well as metal salts such as $ZnCl_2$ and other activating agents can be used [109].

2.6.3 Adsorption Mechanism/Process

Adsorption is a physicochemical process whose mechanism is normally characterized by four steps [110]. (I) migration of solute from the bulk of the solution to the adsorbent surface (bulk diffusion); (II) external mass transfer of solute across the liquid film to the adsorbent exterior surface (film diffusion); (III) solute transport from the exterior surface into the pores of the adsorbent (intraparticle diffusion or pore diffusion) and (IV) adsorption of solute on active sites in inner and outer surfaces of adsorbent. The first step is generally presumed to be rapid and therefore cannot be considered as a rate-controlling step [111].

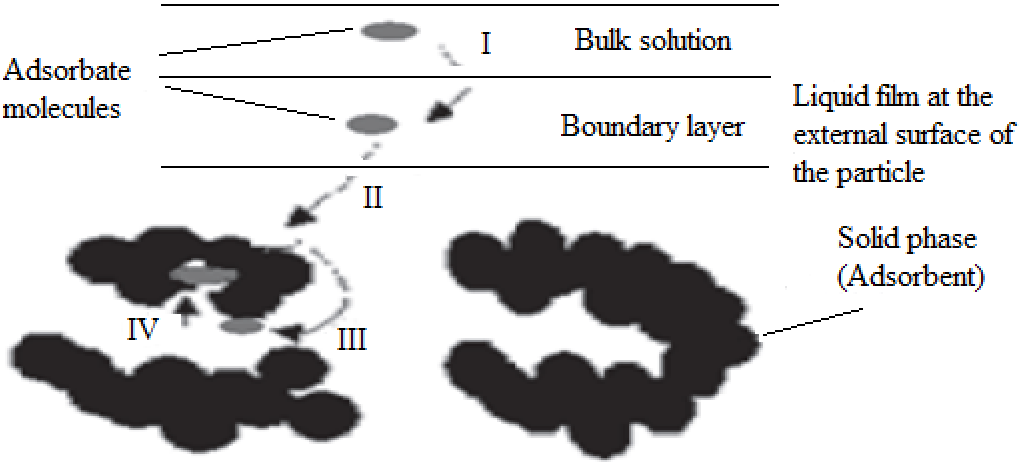

Figure 6: Scheme of the mechanism of molecule adsorption [112].

2.7 Types of Adsorption Phenomena

The adsorption forces between adsorbents and adsorbates are a main factor in defining whether the adsorption is physical or chemical. Occasionally, it is complicated to identify what type of adsorption is predominating in a certain situation, sometimes it might be a combination of chemisorption and physisorption [113].

2.7.1 Physisorption/ Physical Adsorption (Vander Waals Adsorption)

Which is the result of weak intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed, it is reversible and rapid with most valuable parameters of pore sizes, pore structure, pore volume and surface area[114]. It occurs with the development of a multilayer of adsorbate on the adsorbent & the phenomenon decreases with an increase in temperature, usually takes place at a lower temperature which is much below the boiling point of the adsorbate [114] .

2.7.2 Chemisorption/Chemical Adsorption

A specific surface area, types of active sites, number of active sites and stability of active sites are the precondition for chemisorption [115]. Chemical adsorption occurs b/c of a chemical reaction b/n molecules and atoms of the adsorbate with adsorbent. Chemisorption is irreversible for the reason that chemically adsorbed molecules are not able to transfer on the surface within the interface & the advantages are the high selectivity of separation & the capacity to treat [113].

2.8 Factors Influencing Adsorption Process

2.8.1 Contact Time Effect

The time taken by the adsorbent to contact the adsorbate is crucial in wastewater treatment, that is an increase in contact time significantly increases the adsorption capacity of adsorbents as a result of rapid interaction between the adsorbate and the adsorbent material [116]. The rate of adsorption is normally fast in the first few minutes because the adsorbate quickly fills up the readily available adsorption sites. However, in the process of time, equilibrium is achieved and there seems to be no significant adsorption taking place any longer. Numerous researchers have studied the effect that contact time has on the uptake of chromium, reports indicated that equilibrium was reached within 50 min [117], 60 min [118], 90 min [119] and 120 min [120].

2.8.2 pH Effect

The pH value of the metal solution plays a significant role in the whole adsorption process, specifically in the adsorption capacity which mean that the pH of the solution would affect both aqueous chemistry and the surface binding sites of the adsorbents [121]. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged at lower pH, the large number of H^+ ions present neutralizes the negatively charged adsorbent surface and better adsorption is obtained and if the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal/dye ion adsorbed [122].

2.8.3 Concentration Effect

It is widely known that when the initial ion concentration of the adsorbate is decreased the rate of adsorption was increased, however, after a certain time, the rate of adsorption begins to decline as a result of saturation that must have been attained by the adsorbent [123]. Several studies have been published for the optimization the initial chromium ion concentration b/n 10 μg/L and 11 x 10^6 μg/L [124]. Further studies have taken into account the permissible concentration of chromium in wastewater & have reported their findings within the range of ≤ 2000 μg/L [124, 125].

2.8.4 Dose of Adsorbent Effect

When the amount of adsorbent is increased more active sites would be available to which more amounts of metal and dye pollutants can be attached [126]. However, a further increase in the amount of adsorbent would have a negative effect on the adsorption process. This means either the metal adsorption decreases or it becomes steady because the active site for adsorption is blocked by the screening effect [127].

2.9 Adsorption Isotherms

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed & the concentration of the solute in the fluid phase since the adsorption isotherms are important to describe how adsorbates would interact with the adsorbents and it is critical for design and optimizing adsorbent purposes [128].

There are numerous isotherm equations available to analyze the experimental adsorption equilibrium parameters, but the well-known adsorption isotherm models used for single solute systems are Langmuir and Freundlich isotherms are selected in this study to evaluate the adsorption of Cr (VI) and MB on activated carbon derived from the water hyacinth leaf.

2.9.1 Langmuir Adsorption Isotherm

It gave information about whether adsorption is favorable or not. The Langmuir model assumes that the adsorption of heavy metals and dyes occurs as a monolayer on a homogeneous surface by the equilibrium distribution of metal ions & dyes between the solid and liquid phases and the non-linear form is represented by the following equation [129].

$$\frac{1}{\mathrm{qe}}=\frac{1}{\mathrm{kqmaxce}}+\frac{1}{\mathrm{qmax}}$$

Where Ce = the equilibrium concentration of adsorbate in the solution (ppm), qe = the amount of metal or dyes adsorbed per gram of the adsorbent at equilibrium adsorption (mg g^{-1}), K is the Langmuir constant obtained from $\frac{\mathrm{intercept}}{slope}$ and q_{max} is the maximum metal adsorption capacity (mg g^{-1}) or maximum monolayer coverage capacity (mg g^{-1}) obtained from $\frac{1}{\mathrm{intercept}}$; both are i.e. K & q_{max} calculated from the plot $\frac{1}{\mathrm{qe}}$ vs $\frac{1}{\mathrm{ce}}$.

To determine, the Adsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter R_L is defined according to the following equation.

$$R_L=\frac{1}{1+\mathrm{kco}}$$

Where K_L is the Langmuir constant and C_o (ppm) is the initial adsorbates concentration. The R_L value indicates the adsorption process is irreversible when R_L is 0, favorable when R_L is between 0 and 1, linear when R_L is 1 and unfavorable when R_L is greater than one [130].

Langmuir assumptions were made; (a) all sorption sites are uniform, (b) only one sorbate, (c) one sorbate molecule reacts with one active site , d) no interaction b/n adsorbed species [131].

2.9.2 Freundlich Adsorption Isotherm

The isotherm assumes that the process of adsorption is multilayer and occurs onto the heterogeneous surface of the adsorbent process with stronger binding sites [132]. Moreover, increasing adsorption onto binding sites leads to a decrease in the binding strength of the adsorbent. This model is used to estimate the adsorption intensity of the adsorbent towards the pollutant. The Freundlich isotherm equation is as follows [133].

$$\mathrm{qe} = \mathrm{kfce}^{\frac{1}{\mathrm{n}}}$$

Where K_f is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy and n calculated as $\frac{1}{\mathrm{intercept}}$, it is the heterogeneity factor representing the deviation from linearity of adsorbent and is also known as Freundlich coefficient [134].The equation can be conveniently transformed to the following linearized form;

$$\log qe = \log kf + \frac{1}{n} \log ce$$

Where qe is the adsorbate concentration on activated carbon derived from water hyacinth leaf at equilibrium/ the amount of metal or dye adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}), Ce (ppm) is the concentration of adsorbate in solution at equilibrium, K_f and $\frac{1}{\mathrm{n}}$ (slope) are Freundlich constants related to adsorption capacity & adsorption intensity respectively. The higher values of k_f show the greater dependency for adsorbate. The values of $\frac{1}{n}$ between $0 < \frac{1}{n} < 1$ indicate that the adsorption process is favorable & $\frac{1}{\mathrm{n}}$ ranging between 0 and 1 is a measure of surface heterogeneity becoming more heterogeneous as its value gets closer to zero and a plot of *log* qe against *log* Ce gives a straight line with slope $\frac{1}{n}$ and logK_f as intercept [135].

2.10 Adsorption Kinetics

Studies the rate of adsorption and careful examination of the conditions of the experiment affecting the rate of the reaction and the data obtained from this study are fitted into different models like pseudo-first-order and pseudo-second-order among others [136].

2.10.1 Pseudo First Order Model

The pseudo-first-order kinetic model is one of the foremost models used to report the kinetics taking place between the liquid and solid phase in an adsorption process [137] .The non-linear and linear form of the pseudo-first-order kinetic model is expressed by the f/f equation [138].

$$\frac{\mathrm{dqt}}{\mathrm{dt}} = \mathrm{k1(qe - qt)}$$

Where qt is the amount of adsorbate removed at time t in (mg g^{-1}), qe is the adsorption capacity at equilibrium (mg g^{-1}), k_1 is the pseudo-first-order rate constant & t is the contact time (min).

$$ln(qe - qt) = lnqe - k1 \times t$$

It can be rearranged to $log(\mathrm{\ qe - qt}) = \log \mathrm{qe} - \frac{\mathrm{kp1}}{2.303} t$

From the plot of *log* (qe −qt) vs t, k_1 can be determined from the slope.

2.10.2 Pseudo- Second-Order Model

This model is also frequently used in explaining the adsorption kinetics between liquid and solid materials in any adsorption process. Most of the time this equation is used when the first-order model fails [139].

The non-linear and linearized form of the kinetic model is illustrated in the f/f equation[138].

$$\frac{dqt}{dt} = k_2(qe - qt)^2 \qquad \text{(non-linear)}$$

$$\frac{1}{(qe - qt)} = \frac{1}{qe} + k_2 t \qquad \text{(linearized)}$$

Where qt is the amount of adsorbate removed at time t (mg g^{-1}), qe is the adsorption capacity at equilibrium, K_2 is the pseudo-second-order rate constante determined from the intercept of the plots of t/qt against t and t is the contact time (min).

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$$

3 MATERIAL AND METHODS

3.1 Study Area

Bahir Dar City is located in North Western Ethiopia approximately 565 km from Addis Ababa, which is the capital city of Amhara National Regional State (ANRS). The Experiment was conducted at the Department of Industrial Chemistry, Bahir Dar University. The adsorbent material was collected from Abay River and the wastewater were also collected from Bahir Dar tannery & textile industry in Bahir Dar, Ethiopia.

3.2 Instrument and Equipment

The apparatus and equipment that have been used during this research work are mentioned below. To investigate the crystallinity structure of the ACDWHL, XRD (X-ray diffractometer, XRD7000(2θ angles) using Cu kα radiation (λ=1.54 Å or 0.154nm), scanning speed = 0.03(degree/min)) has been employed. To determine the concentration of Cr (VI) and MB UV – Vis-spectrophotometer (UV–Vis, DR–6000) was used. To determine the specific surface area, pore volume and pore diameter of a material, BET (Brunauer-Emmett-Teller (BET) /NOVA – 4000E)) analysis has been done & the material to be analyzed was first degassed (heating to a temperature of 77.35°k and kept for a minimum of 103.2min) in the presence of nitrogen to eliminate moisture and carbon dioxide that may be present. To determine the availability of the functional groups on the surface of ACDWHL FTIR (FTIR Spectrometer, JASCO) (scanned over the range of 400-4,000 cm^{-1}) has been carried out. pH meter, Digital electronic balance, Drying Oven (India advanced technology Inc) name, Furnace (ME2.5-12GJ China), Magnetic stirrer, Pipettes, spatulas, Erlenmeyer flask, beaker, test tube, mortar and pestle, glass rod, volumetric flask and different types of beakers was used.

3.3 Chemicals and Reagents

The chemicals and reagents that have been used during this experimental work are: 1,5 diphenyl carbazide (98% purity), deionized water, potassium dichromate (99.7% purity), hydrochloric acid (37% purity), potassium hydroxide (85% purity), sulphuric acid (98% purity), acetone (99.9%), methylene blue dye (99.9% purity), zinc chloride (99.9 % purity) and sodium chloride (99.5%

purity was used for the determination of points of zero charge). All chemicals used in this study were analytical grade and used without any further purification.

3.4 Methods

3.4.1 Sample Collection and Preparation

3.4.1.1 Collection and Preparation of Real Contaminated Water Samples

The wastewater samples were collected from Bahir Dar tannery and textile industry from pre-treatment and post-treatment sites, which are located around Bahir Dar City, Ethiopia. As one of the objectives of this study was to make recommendations on the treatment effectiveness of the wastewater treating mechanism used by the tannery and textile with respect to the content of chromium and methylene blue, the samples were collected from two sites, i.e., from pre-treatment site and post-treatment site. Figure 7 show the photograph captured during the collection of the pre- treatment and post -treatment tanning samples site. Figure 7a shows the sample was the sample collected from the release point of the tanning and textile process as the effluents were eliminated from the tanning and textile tank before it gets diluted as it mixes with the wastes of other processing components. The effluent has a characteristic of dark-green color (which maybe, an indication that the sewage contains chromium) and unpleasant odor whereas MB effluent has a blue like mud or dust color.

Figure 7: a) the pretreatment, b) post-treatment of the real tanner wastewater sample.

The sample which was collected at the outlet of the wastewater is shown in figure 7b. This site of sample could be called as post-treatment site. The color of the sample collected from tannery was partially different from the pre-treatment site sample i.e., its color was not dark-green; its color like a color of water mixed with mud or dust in addition to its odor was bad (hydrogen sulphide smell) even after days as it was being kept in the laboratory. But the color of methylene blue after-treatment was like water color.

3.4.1.2 Real Sample Preparation for UV–Vis, Analysis

The wastewater was collected by a polyethylene container, that is pre-washed with diluted nitric acid (0.1M), and immediately transported to the laboratory for the experiment. To determine the concentration of Cr (VI) and MB in the effluent of tannery and textile the wastewater was firstly sedimented to remove the suspending ingredients(figure 8a). Then the upper part of the suspension and suspended solid of the effluent was filtered using the Whatman (11µm) filter paper[140, 141] (figure 8b). The same procedures have been followed for both samples of pre-treatment and post-treatment sites. The preparations were made in different conical flasks simultaneously. We took 50 mL solution in each batch (pre-treatment and post-treatment) and added the optimized amounts of dose = 150 and 206 mg, time = 120 & 90 min, pH = 2 and 10 was used to test the efficiency of the adsorbent in the real samples of Cr (VI) and MB, respectively. To determine chromium (VI) selectively, 50 mL of a sample of pre-treatment and post-treatment were taken into a separate 250 mL volumetric flasks and then, 2 mL of 2 M H_2SO_4 and 1 mL 1, 5-Diphenylcarbazide solutions were added to each flask[142]. The solutions were allowed to stand for about 10 min until it develops color.

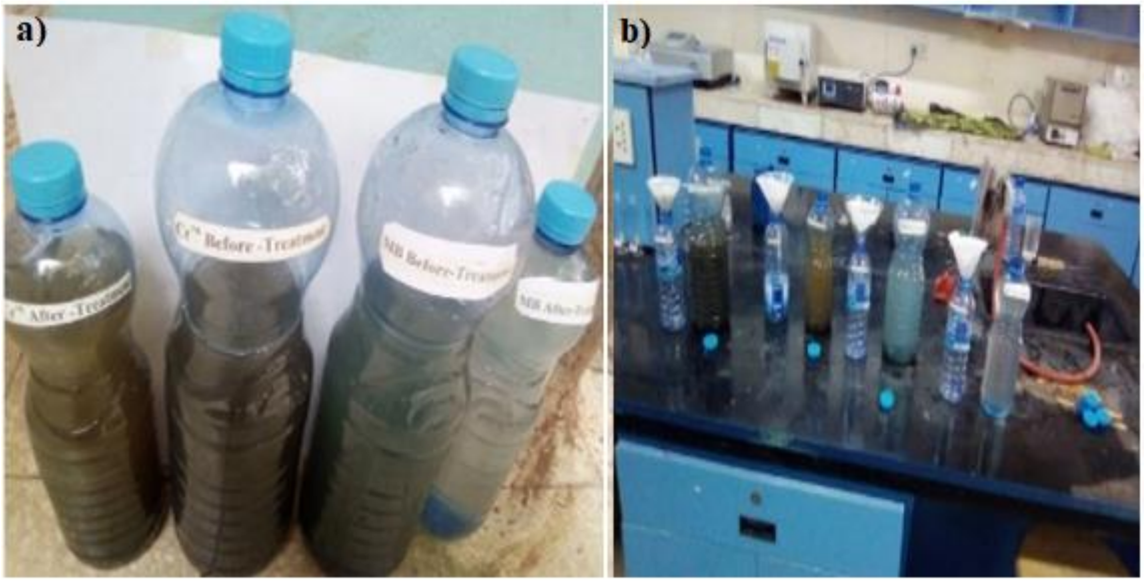

Figure 8: a) Sample sedimentation, b) Samples filtration from tannery & textile effluents .

3.4.1.3 Preparation of Standard, working and Stock Synthetic water samples

Potassium dichromate ($K_2Cr_2O_7$) and methylene blue ($C_{16}H_{18}ClN_3S$) was used as the source for stock solution. The standard stock solution of both chemicals was (1000 ppm) which was prepared by dissolving 2.828 g $K_2Cr_2O_7$ [143] and 0.5% MB, respectively in 1000 mL of distilled water. Standard solutions (for calibration) of potassium dichromate and methylene blue with different concentrations were prepared from the stock solution by appropriate dilutions, that is [0 (blank),1, 5, 10, 15, & 20] ppm in 50 mL volumetric flask up to the mark for each (figure 9 a and b).

For potassium dichromate a series of five standards containing [1, 5, 10, 15 & 20] ppm was prepared in 50 mL volumetric flasks and acidified with 2 mL of 2M H_2SO_4. Then a freshly prepared 1 mL of 1, 5–Diphenyl carbazide was added to each standard. Pink color was formed immediately in which the intensity of the pink color was increased with concentration. Figure 9 shows a series of standard solutions ready for color comparisons in the analysis using color comparison and for calibration curve construction in the analysis of the analyte by UV-visible spectrophotometer. A graph of absorbance versus concentration of the standards (calibration curve) was displayed under the section of results and discussion.

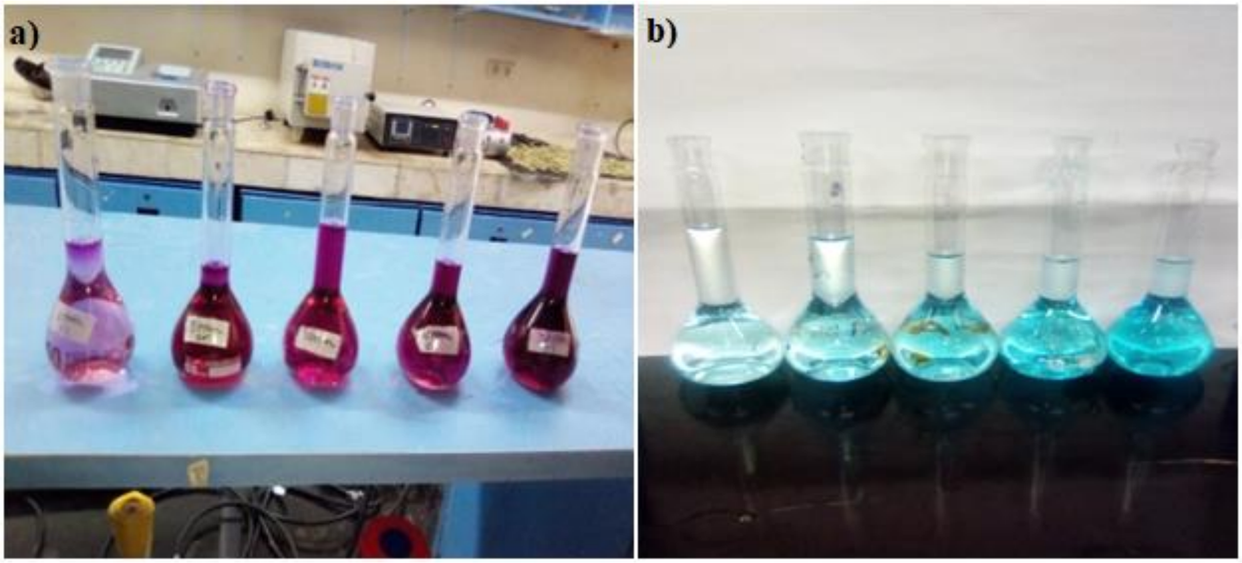

Figure 9: A Series of standard solution for Cr(VI) a) and MB b**)**.

In order to make a solution of 1, 5-Diphenylcarbazide, 250 mg of 1, 5-Diphenylcarbazide powder was placed into a 100 mL volumetric flask and completely dissolved with acetone before being entirely filled with distilled water [53]. For each experiment, a freshly produced dye (that is DPC) has been used. The prepared dye was covered with aluminum foil to prevent it from the exposure of sunlight. The concentration of the working solution of potassium dichromate and MB has been prepared by diluting the standard solution and it becomes; 2, 4, 6, 8 & 10 ppm in 50 mL volumetric flask and filled with water up to the mark.

3.4.2 Preparation and Characterization of Adsorbent Material

3.4.2.1 Preparation of Adsorbent

Figure 10: Water hyacinth taken from the Abay River.

The activated carbon was prepared from the water hyacinth leaf which was brought from the Abay river (figure 10 a and b). Firstly, the water hyacinth leaf was cut into pieces and washed with tap water several times followed by drying it with sunlight for four days. Again, the dried water hyacinth leaf pieces were washed with deionized water several times and dried in an oven at 110 ^{o}C for 12 hr. Then, the dried water hyacinth leaf was carbonized at 400 ^{o}C, 500 ^{o}C & 600 ^{o}C for 2hr, in a muffle furnace. After carbonization process it was cooled down overnight, (then impregnate with 1:1 ratio (w/w) for each temperature and tested the efficiency to select the optimum temperature for the next steps). Three different impregnation ratios of $ZnCl_2$ solution were used to impregnate the carbonized sample which was $ZnCl_{2:}$ carbonized sample (w/w) that is (1:1, 2:1 and 1:2). Then, the solution was stirred & heated at 80 ^{o}C for 2 hrs, and it was then left for 24 hr, at room temperature to increase rate of activation.

The settled down solution was filtered to remove the excess activating agent . Subsequently, it was washed with 1M HCl solution to remove zinc and other species followed by washing several times with distilled water. The obtained material was dried in an oven at 110°C for 12 hrs. Finally, it was heated at 700^{0}C for 2 hrs that is to increase the activation sites. The prepared material (ACDWHL) was ground using mortar and pestle. The powdered material was packed with plastic bag for further steps.

3.4.2.2 Characterization of Activated Carbon Derived from water hyacinth leaf

Basic physical characteristics of ACDWHL such as moisture content, volatile matter, carbon yield and ash content were examined. The XRD and FTIR were used to study the crystal structure and functional groups of ACDWHL, respectively. The BET was used to determine the surface area, pore volume and pore size of ACDWHL.

3.4.2.3 Moisture Content (Mc)

The moisture content was determined by loss on drying method 2000 mg of equally grinded ACDWHL was accurately weighted and placed into a clean crucible of a known weight. Then the crucible containing with a known weight of the ACDWHL was incubated at 110^{o}C in an oven.

After 8 hrs, the weight of the ACDWHL and the crucible was weighted and finally, moisture content was calculated using the following equation [144].

$$\text{Mc (\%)} = \frac{WB - \text{WA}}{WB} \times 100$$

Where M_c is the moisture content of the ACDWHL in percentage, W_B is weight of the sample before drying and W_A is weight of the sample after drying.

3.4.2.4 Ash Content (Ac)

The ash content of the ACDWHL was determined by weighting 2000 mg of ACDWHL and placed in dried crucible. The crucible containing the sample was put in to a muffle furnace at temperature of 500^{o}C for 1:30 hrs. Finally, the crucibles removed from the furnace and ACDWHL sample was weighed and the percent of ash content calculated by using the following equation [144].

$$\text{Ac (\%)} = \frac{\text{WB} - \text{WA}}{\text{WB}} \times 100$$

Where A_c is ash content in percent, W_B is weight of the ACDWHL sample before heating and W_A is weight of the sample after heating.

3.4.2.5 Volatile Mater (Vm)

2000 mg of the ACDWHL sample was taken and placed in a dried crucible and heated in a muffle furnace adjusted at 700°C for 10 min. Then the crucible was cooled and weighed. Finally, the volatile matter of the ACDWHL was calculated by using the following equation [145].

$$Vm \text{ (\%)} = \frac{\text{WB} - \text{WA}}{\text{WB}} \times 100$$

Where V_m (volatile matter of the ACDWHL in percentage), W_B is (weight of the ACDWHL sample before heating) and W_A is (weight of the sample after heating).

3.4.2.6 Carbon Yield (Y)

Carbon yield is the ratio of weight of the sample after carbonization (4.63g) to the weight before carbonization (8.0g) and it tells us how much of the precursor is changed through the carbonization process. The Carbon yield were calculated by using the following formula.

$$Y = \frac{WA}{WB} \times 100$$

Where: Y (Carbon Yield), W_B (was dried weight before carbonization) and W_A (was the dried weight of water hyacinth leaf after carbonization).

3.4.2.7 Point of Zero Charge (pHpzc)

The point of zero charge (pHpzc) of the activated carbon was a function of pH and it is a pH at which the charge of the solid surface is zero and the adsorbent would be positively or negatively charged below or above pHpzc value respectively and expected to adsorb anionic and cationic charged species [146]. The point of zero charge (pHpzc) of the activated carbon was determined by the solid addition method [147]. To determine the point of zero charge of ACDWHL, 0.1 M of NaCl solution with the initial pH values ranging from 1 to 12 was prepared. The pH was adjusted by using 0.1 M HCl and 0.1 M KOH solution. Then, 200 mg of ACDWHL was added to each solution and it was covered immediately with aluminum foil. The mixture of the solution was shaken for 3 hrs and settled down for 24 hrs [146]. Then the solutions were filtered. The final pH values of all solution were measured and ΔpH was made by subtracting the initial pH from the final pH values. The graph was plotted by using the initial pH values against ΔpH. From the plotted graph a point of intersection of the resulting curve `with the X-axis has given the pHpzc value [146].

3.4.3 Determining the Concentration of Cr (VI) & MB by using UV-Vis

UV-Vis spectrophotometer investigation has been carried out to determine the concentration of chromium & methylene blue before and after the addition of ACDWHL. The UV-Vis was calibrated between 1 ppm – 20 ppm (with 5ppm difference). The maximum wavelength was: λmax = 543 nm & 664 nm for chromium & methylene blue respectively. To determine the concentration of Cr (VI) the following methodology was used. Firstly, 250 mg of 1, 5- diphenyl carbazide was dissolved in 50 mL acetone solution, then, 2 mL of 2 M H_2SO_4 (The acid is required because the dye can bind to chromium more effectively in an acidic environment) and 1 mL of diphenyl carbazide have been added[53]. Finally, the UV-Vis measurement has been done to determine the concentration of Cr (VI) at 543 nm.

3.4.4 Determination of the Adsorption Efficiency of the ACDWHL

Batch methods were used to measure the adsorption at room temperature. The batch adsorption experiments were carried out at a desired pH value, contact time, initial concentration and adsorbent dose. The pH of the solution was adjusted by adding 0.1M of HCl and 0.1M KOH. Then, 200 mg of ACDWHL was added into a flask containing 50 mL of potassium dichromate and methylene blue solution separately. The solution was stirred for desired time with 200 rpm at room temperature. The concentrations of Cr (VI) and MB were determined after filtration. Adsorption efficiency of chromium and MB adsorbed per gram of adsorbent were calculated using the following equations respectively[148]. The final result used to plot the graph.

$$\% \text{ R} = \frac{\mathbf{Co-Cf}}{\mathbf{Co}} \times 100$$

Where; *%R* is percent removal, *Co* is initial concentration and *Cf* concentration after adsorption

$$\text{qe} = \frac{(\mathbf{Co-Cf})\times \mathbf{v}}{\mathbf{m}}$$

Where *qe* is metal removal in mg g^{-1}, *Co* is initial concentration, *Cf* concentration after adsorption, *m* is adsorbent mass in gram and *v* is volume of solution used during the experiment.

3.4.5 Optimization of the Batch Adsorption Experiment

All batch adsorption experiments were conducted at room temperature. For the batch experiment 50 mL of known chromium (VI) and methylene blue with known adsorbent dose which are 50–250 mg were placed in a 250 mL volumetric flask. The pH of chromium (VI) (1-8) and for methylene blue (6-14) was used. The pH was adjusted using 0.1 M HCl and KOH. The solution was placed on a magnetic stirrer at room temperature followed by stirring at 200 rpm for about 30 min – 180 min.The concentration of Cr (VI) and MB was measured using UV-Vis spectrophotometry at 540 nm and 664 nm, respectively.

3.4.6 Parameters Affecting the Adsorption

3.4.6.1 Effect of pH

The adsorption of chromium (VI) and methylene blue depends on the solution pH which influences the electrostatic binding of ions to correspondent metal and dye groups. Change in pH influences the adsorption process through isolation of functional groups as the active sites on the surface of the adsorbent. The optimization of pH is necessary, so the effect of pH was studied in the range of 1-8 and 6-14 for chromium (VI) and methylene blue, respectively. For this purpose, 50 mL of the working solution (10 mg/l) was poured into different volumetric flasks and pH was adjusted from 1 – 8 & 6 – 14, (1, 2, 3, 4, 5, 6, 7, 8 & 6, 8, 10,12,14 respectively for chromium (VI) and MB) by adding 0.1M HCl and 0.1M KOH drop wise. Then the selected dose of 200 mg adsorbent was added and agitated at 200 rpm for 90 min. Finally, the remaining chromium (VI) and methylene blue concentration was analyzed in the filtrate and one optimum pH value was selected for each at which the maximum removal occurs.

3.4.6.2 Effect of Dose

The effects of adsorbent doses were studied at optimum pH (2 & 10) on chromium (VI) and methylene blue by varying the adsorbent dose in milligrams of 50, 100, 150, 200 and 250 mg. The experiment was carried out by measuring 50 mL of the working solution contains 10 mg/L of the initial concentration of chromium (VI) and methylene blue into 250 mL of flask. The pH was adjusted using 0.1M KOH or 0.1M HCl and agitated with 200 rpm at 90 min. The mixture was filtered immediately through a Whatman filter paper. Finally, the filtrate was analyzed to evaluate the amount of chromium (VI) and methylene blue adsorbed on ACDWHL by using UV-Vis spectrophotometry at 540 nm and 664 nm, respectively. The Chromium (VI) was specifically tested with a complexing agent which was called 1, 5 DPC.

3.4.6.3 Effect of Concentration

To study the effect of the initial concentration of chromium (VI) and methylene blue, experiment was conducted by considering all the parameters keep at the optimum value and by changing the initial concentration of chromium (VI) and methylene blue. The experiment was performed by using 200 mg adsorbent dose loaded into 250 mL volumetric flask containing 50 mL of chromium (VI) and methylene blue working solution with initial concentration of (2, 4, 6, 8 & 10 ppm). The pH of the solution was adjusted using 0.1M KOH and 0.1M HCl. The solution was agitated at 200 rpm for 90 min. The mixture was filtered immediately. Then the filtrate was analyzed to evaluate the amount of chromium (VI) and methylene blue adsorbed on ACDWHL by using UV-Vis spectrophotometer at 540 nm and 664 nm, respectively. In this step, 1, 5-DPC was also used as a complexing agent for Chromium (VI).

3.4.6.4 Effect of Contact Time

The effect of contact time was studied by varying the agitation time from 30, 60, 90, 120, 150, and 180 min. The experiment was carried out by measuring 50 mL of the initial working chromium (VI) and methylene blue solution with a concentration of 10 ppm in 250 mL volumetric flask. The solution was adjusted to the optimized pH using 0.1M KOH or 0.1M HCl with a dose of (200 mg) ACDWHL was added to each flask and then agitated at optimum speed 200 rpm. The mixture was filtered and then the filtrate was analyzed to evaluate the concentration of chromium (VI) and MB adsorbed on ACDWHL by using UV-Visible spectrophotometer at 540 and 664 nm, respectively. For Cr (VI), the complexing agent was 1, 5- DPC.

3.4.7 Adsorption Isotherm

To study the adsorption isotherms the optimum conditions which were found from previous optimization experiments was applied only by varying initial concentration of chromium (VI) and methylene blue. These experiments were carried out using adsorbent initial concentration in the range of 2 ppm to 10 ppm with a 2-ppm difference. For each adsorbent initial concentration 50mL of sample was taken at optimum conditions. The data from the experiment were fitted into Langmuir and Freundlich [149].

3.4.8 Adsorption Kinetics Study

Kinetic study of the adsorption was conducted at constant ACDWHL dose, pH, chromium (VI) and methylene blue concentration and agitation speed with different time. This study was done by taking 50 mL of chromium (VI) and methylene blue working solution which contains 10 ppm of chromium (VI) and methylene blue concentration in a separate set of flasks of 250 mL capacity and the adsorbents were added to these at an optimal dose of 150 and 200 mg chromium (VI) and methylene blue). The sample were adjusted to optimum pH (2 &10) using 0.1M of KOH or 0.1M HCl and shaken on a shaker at 200 rpm. The experiments were carried out for the duration of agitation time (30, 60, 90,120, 150, and 180 min), after the formation of equilibrium, filter and analysis using a UV-Visible spectrometer. For the kinetics of chromium (VI) and methylene blue adsorption on ACDWHL, two kinetic models were applied. These were pseudo-first order kinetics and pseudo-second-order kinetics. The agreement between the model's predicted values and experimental data were expressed by the correlation coefficients (R^2). The model with a relatively high correlation coefficient value is fit for describing the adsorption kinetics process [150].

4 RESULTS AND DISCUSSION

4.1 Characterization of the Adsorbent

4.1.1 Proximate Analysis of the Activated Carbon

The proximate analysis of the activated carbon obtained from water hyacinth leaf was done in order to identify its moisture content, volatile matter, ash content and carbon yield of activated carbon produced. The proximate analysis was carried out using an oven and muffle furnace. The result obtained is shown in table 2. The detailed calculation was also indicated in appendix 7B.

Table 2 Proximate analysis of activated carbon (ACDWHL).

Proximate analysis	Mass in % after proximate analysis
Moisture	6.3 ± 1.26
Volatile mater	27.3 ± 3.2
Ash content	11.2 ± 1.259
Carbon yield	56.4 ± 1.4

A small amount of moisture and ash content is better for chemical treatment because sample with higher moisture content needs more heat to evaporate the moisture [151]. High ash content also affects the chemical treatment which would reduce the overall activity of the adsorbent. This implies that, the lower the ash content, the better material for chemical treatment. The moisture content for ACDWHL recorded was 6.3 ± 1.26. The result coincides with the Plantain (Musa paradisiaca) fruit stem 7.33 ± 1.5 % of moisture content that has been reported previously [144].

This concludes that the prepared activated carbon has a good quality. As the content of the moisture is lower, the effectiveness of the adsorbent is becoming higher, this is due to water molecules would have the potential effect of filling the adsorbent binding site before it contacts with the solution (adsorbate), this reduces the efficiency of the activated carbon. Therefore, the prepared activated carbon produced was stored in air tight bag, otherwise it might adsorb moisture content from the environment. The volatile matter and carbon yield of the ACDWHL was 27.3 ± 3.2 & 56.4 ± 1.4, whereas the ash content was 11.2 ± 1.259. The ACDWHL has higher volatile matter content (showed that some of the organic molecules of the material was attacked and it is important for adsorption experiment) and low ash content of a biomass resource makes it a good material or activated carbon. For example, from the previous report, activated carbon obtained from Plantain (Musa paradisiaca) fruit stem shows 31 ± 6.08 % of ash content and 32.33 ± 1.15 % volatile mater [144]. The volatile mater and ash content values obtained from ACDWHL is desirable for the adsorption of Cr (VI) and MB. Generally, the lower the ash value, the better the activated carbon for use as an adsorbent [144].

4.1.2 Effect of Activation Process on the Preparation of Activated Carbon

The carbonization of the material was done at 400, 500 and 600°C for 2hr. After the carbonization, the obtained material was mixed with the activating agent ($ZnCl_2$) with 1:1 ratio. The mixture was heated at 700^0C for 2 hr, to enhance the activation sites of the material. Finally, the percentage removal of the material obtained at the three temperatures was performed by removed Cr (VI) in the 10 ppm solution and the result obtained at 400, 500 and 600^oC was 61,73.6 & 71.5% .

The lower efficiency at 400 ^{o}C was due to the incomplete combustion of the material, which reduces the active sites. Moreover, the lower efficiency of the material at 600 ^{o}C compared with 500 ^{o}C would be the decomposition of the functional groups that would interact with Cr (VI) that are available in the material.

Therefore, based on the results obtained the carbonization temperature at 500°C was selected for subsequent experiments. For the preparation of activated carbon, three impregnation ratios have been used and as the result is summarized below.

Table 3 Effect of impregnation ratio in the activated carbon preparation.

Trial	**Impregnation Ratio (ZnCl₂ : carbonized material)**	**Temperature**	**Time**	**%Removal**
1	1:1	500°C	2 hrs	74
2	2:1			71.65
3	1:2			75.5

4.1.3 Point of Zero Charge (pHpzc)

The point of zero charge (pHpzc) is defined as the pH of the mixtures at which surface charge on the material is zero (the surface of material has net electrical neutrality) and its value was determined by the solid addition method [147]. The pHpzc values for the activated carbon (ACDWHL) was 5.4. The pHpzc value at 5.4 indicates that the ACDWHL surface has the presence of acid functional groups. In addition, the values of pH < 5.4, implies that the dominancy of acidic functional groups compared with the basic. The positive charge on the surface of the ACDWHL could be obtained at pH below the pHpzc value and the negative charge on the surface of the ACDWHL could be obtained at pH levels above the pHpzc value. A positive charge of ACDWHL favorable to the uptake of negative charge (anionic) species on the other hand negative charge of ACDWHL favorable to the uptake of positive charge (cationic) species. During the study of adsorption test, the investigation of the pHpzc value would help to select the pH value of the medium. Hence the percent adsorbent removal capacity increased below and above pHpzc value for anionic and cationic species [147]. Figure 11 Show the point of zero charge (pHpzc) of the activated carbon derived from water hyacinth leaf was 5.4 and at this point the surface of ACDWHL is neutral but below and above this point the surface of ACDWHL is positively and negatively charged respectively which attracts the negatively charged chromate ion and the positively charged methylene blue ion and this results the increasing of adsorption.

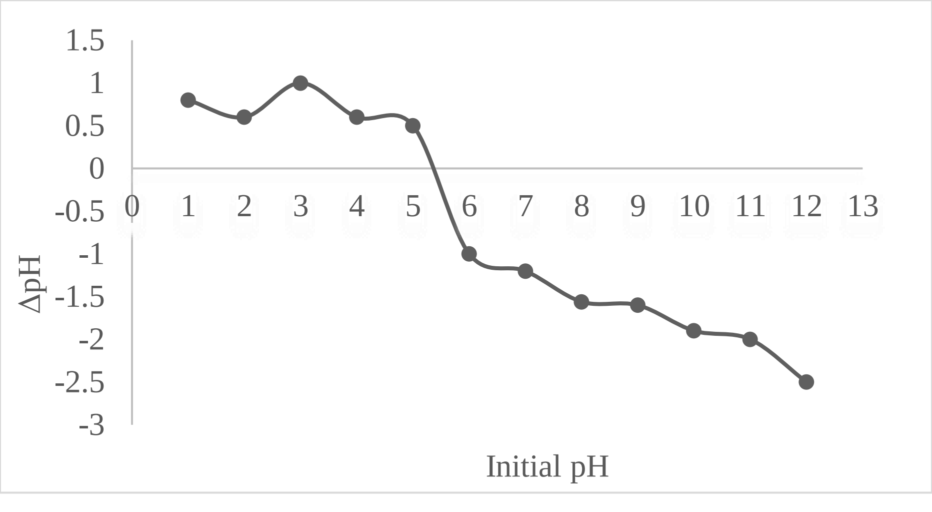

Figure 11: Point of zero charge (pHpzc) of the ACDWHL.

4.1.4 FT-IR Analysis

The spectra of activated carbon derived from water hyacinth leaf before and after the adsorptions of Cr (VI) and MB ions were used to detect changes in the vibration frequencies of the functional groups. Figure 12 shows the FT-IR spectra of the activated carbon derived from water hyacinth leaf. The spectra of adsorbent were measured between wave number ranges from 400-4000 cm^{-1}. The functional groups such as carboxyl (COOH), amine (–NH_2) and hydroxyl (OH^-) have the main role in absorbing Cr (VI) and MB specially hydroxyl, amine, C═O and C─O groups are the main effective on adsorption of Cr (VI) and MB ions. The broad band in the region around 3423 cm^{-1} is corresponding to the surface hydroxyl of bonded carboxylic acid and (–N–H) groups [152]. The O–H stretching vibrations present within a broad range of frequencies indicates; the presence of bonded O–H bands in carboxylic acid group on the surface of ACDWHL. The peak at 2356 cm^{-1} was associated with existence of C≡N (nitriles) [53].The peaks at about 1615 cm^{-1} could be due to C=O stretching of carbonyl group, which suggests carboxylic acid [153]. The peak at about 1039 cm^{-1} corresponding's to the stretching vibration of C–O, C–N or C–H group in carboxylic acid, amine and alcohol [152]. Both of the hydroxyl and carboxylic acid functional groups present in the structure of the adsorbent can be achieved by deprotonation and protonation making it to interact with metals and dyes easily and therefore may be the major adsorption sites for the removal of hexavalent chromium and MB ions from solutions [152].The FTIR spectrum of the activated carbon derived from water hyacinth leaf obtained after the adsorption of chromium (VI) and MB ions is shown in figure12. The FT-IR spectrum of ACDWHL before and after adsorption shows, shift in wave number and intensity. Before adsorption of chromium (VI) and MB ion there was a peak formation at a wave number 3423,2356,1615 and 1039cm^{-1}. After chromium (VI) and MB adsorption the peaks shifted to 3439, 2352, 1615 and 1087 cm^{-1} for chromium (VI) and 3447,2369,1638 & 1046 cm^{-1} for MB. These shift in wave number show that the hydroxyl, amine, carbonyl and carboxylic group involved in the adsorption of chromium (VI) and MB ions. Therefore, the functional groups of OH^-, C≡N– H, C=O, –N–H and –CH groups in water hyacinth leaf would participate to interact with chromium (VI) and MB ion, involving the mechanism of surface complex, hydrogen bonding and electrostatic attraction.

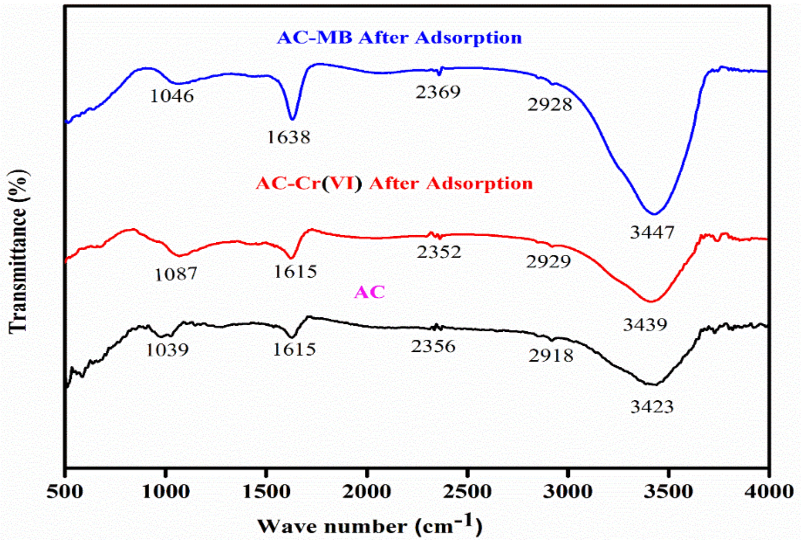

Figure 12: FTIR analysis of ACDWHL before and after adsorption of Cr (VI) & MB.

4.1.5 XRD Analysis

X-ray Diffraction (XRD) analysis was carried out to study the crystalline structure of the material prepared. The XRD-result of ACDWHL, ACDWHL-Cr and ACDWHL-MB is shown in Figure 13. For ACDWHL, the observed peaks were at 32˚, 34.7˚, 36.5˚, 47.9˚, 56.8˚, 63.2˚ and 68.2˚, which indicate that the presence of graphitic carbon in ACDWHL. XRD analysis of ACDWHL-Cr and ACDWHL-MB after the adsorption, which shows a formation of a sharp peaks, change in intensity of peaks that is some peaks are decreased and some are constant and also there is a shifting of angles which confirms the adsorption of chromium (VI) and MB ions by ACDWHL.

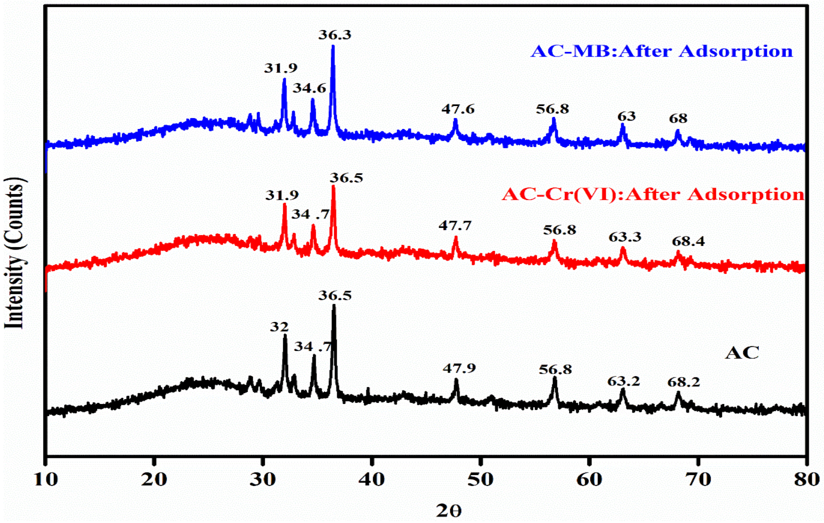

Figure 13: XRD analysis of ACDWHL before and after adsorption of Cr (VI) & MB.

4.1.6 BET Surface Area Measurement

Surface area, pore size and pore volume are the three significant physical properties that affect the quality of adsorbents. The adsorbents with smaller pore size have a higher capacity in the adsorption process with large exterior surface. The adsorption increases as the adsorbent size decreased, because the surface area increases when the adsorbents size decreases. There are three classifications of the pore size of a material shown in table 4.

Table 4 Pore classification on the basic of pore diameter.

Types of pores	Diameter
Micropores	DP < 2 nm
Mesopores	2 nm ≤ DP < 50 nm
Macropores	DP ≥ 50 nm

The BET surface area of ACDWHL, pore volume and average pore diameter were observed to be 616.387 m^2 g^{-1}, 0.2064 cm^3 g^{-1} and 0.2261nm respectively, from this the pore diameter of ACDWHL indicating that the formation of micro pore diameters. The resulting large surface area was in the range (500-1500 m^2/g) [87]. So, the higher the surface area the better the adsorption performance of ACDWHL [154]. Therefore, the BET analysis of the selected adsorbents would assist Cr (VI) & methylene blue, adsorption capacity or adsorption studies.

4.2 Effect of Adsorption Parameters

4.2.1 Calibration Curve Plotted for Chromium (VI) & Methylene Blue Adsorption

The calibration curve plotted for chromium (VI) and methylene blue at a wave length of 543 and 664 nm respectively were obtained from standard solutions of potassium dichromate and methylene blue with different concentrations and the corresponding absorbance result is shown in table 5. It is important to determine the unknown concentration of Cr (VI) and MB.

Table 5 The Cr (VI) & MB standard concentration with absorbance.

Initial concentration (ppm)	Absorbance	
	chromium (VI)	Methylene blue
1	0.545	0.12
5	1.028	0.5
10	1.322	0.92
15	1.657	1.36
20	2.035	1.78

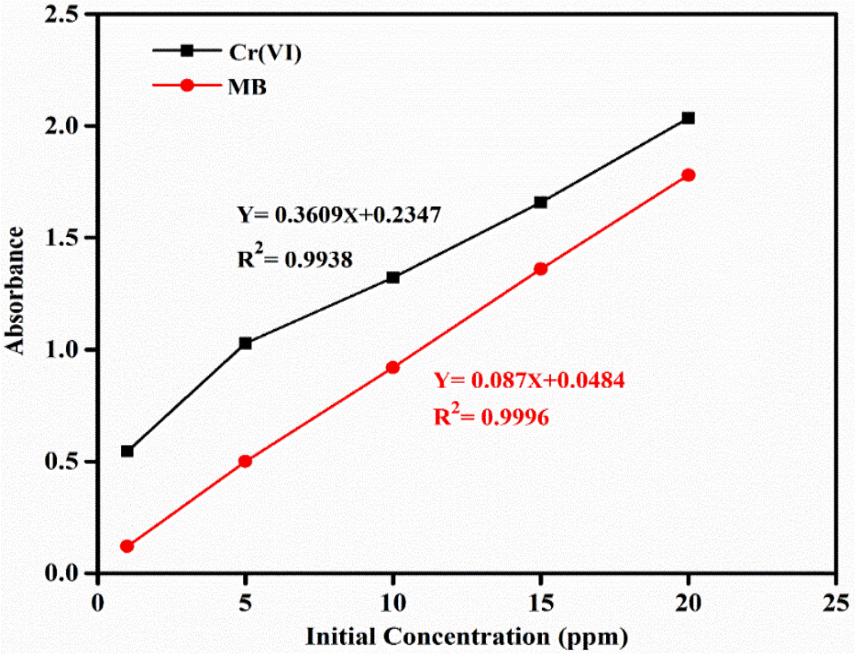

Figure 14: Calibration curve for hexavalent chromium & methylene blue solution.

4.2.2 Effect of pH on Chromium (VI) & MB Adsorption

The effect of pH on the adsorption of chromium (VI) & MB by ACDWHL was carried out with the pH range from 1-8 and 6-14, respectively. To run this parameter: adsorbent dose = 200 mg, contact time= 90 min, initial concentration = 10 ppm and stirring speed =200 rpm was taken as constant for both adsorbates.

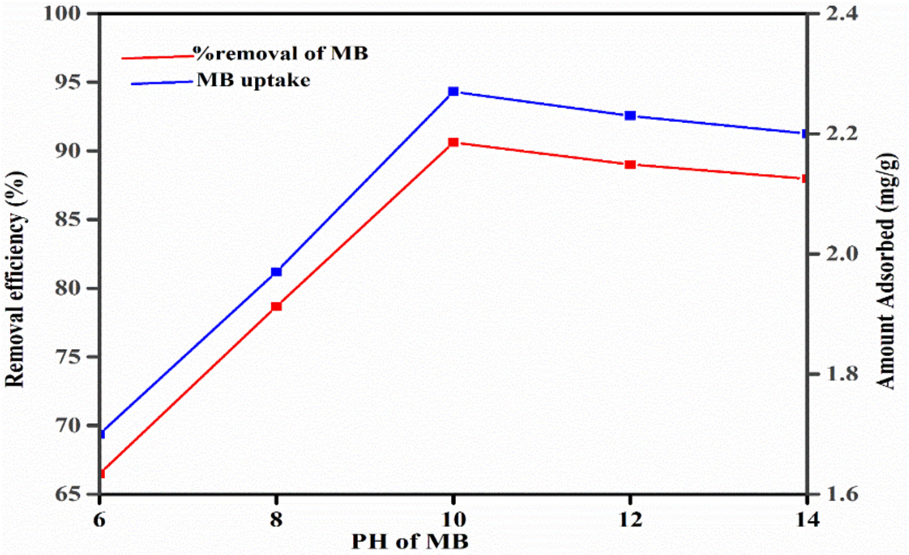

Figure 15: Effect of pH on MB removal by ACDWHL.

Figure 15, shows that difference in the percentage removal of the MB dye from aqueous solution with ACDWHL, (pH = 6 – 14). The percentage removal of MB dye significantly increased from 66.48 % to 87.97 % as the solution pH increased from 6 to 14. This shows that the basic medium is more favorable than the acidic medium for the adsorption of MB dye. The high pH value indicating that the OH^- ion concentration increasing through the surface of ACDWHL. This leads to exist a strong electrostatic attraction between the positively charged cationic dye and the ACDWHL, which results in maximum adsorption of the MB dye.

On the other hand, decreasing in pH value leads to increase in the number of positively charged sites on the adsorbent surface(ACDWHL)[155]. Hence, the positively charged surface of ACDWHL doesn't favor for the adsorption of cationic dyes. This is due to presence of electrostatic repulsion between the positively charged cationic dye molecules and the adsorbent surface leading to have lower adsorption of the MB dye. Finally, we deduced that pH = 10, is taken as the optimum pH value, since percentage removal didn't show any significant increment above or below pH = 10. At pH = 10 the percentage removal of MB was 90.62%.

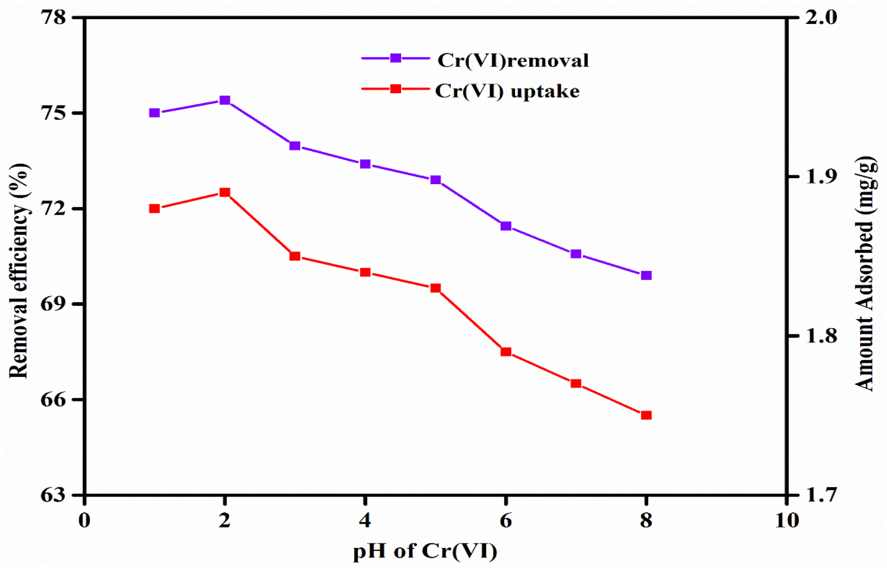

Figure 16: Effect of pH on Cr (VI) removal by ACDWHL.

The removal efficiency of the ACDWHL for Cr (VI) was higher at pH = 2 as shown in figure 16. After pH = 2 the removal efficiency was decreased and at pH = 8, minimum removals efficiency of ACDWHL was recorded. The removal efficiency of ACDWHL was decline from 75 % to 69 % when the solution pH increased from 2 – 8. The reason behind to this is that at lower pH value adsorbent can easily protonate and generate positive net charge. The existence of large number of H^+ ion at this pH value on the adsorbent surface that outcomes in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions [156]. As the pH increased dual competition of both the anions (OH^- and CrO_4^{2-}) to be adsorbed on the surface of adsorbent. This indicates that ACDWHL is acceptable for the removal of chromium (VI) from aqueous or industrial effluent solution under acidic condition. Depending on the pH of the predominant species present, H_2CrO_4 exist at pH less than about 1, $HCrO_4^-$ and $Cr_2O_7^{2-}$ at pH between 1 and 6 and CrO_4^{2-} at pH above 6 [130]. This result clearly shows that the active form of chromium (VI) that can be adsorbed by the activated carbon resulting from water hyacinth leaf was $HCrO_4^-$ & $Cr_2O_7^{2-}$. Removal of chromium (VI) at different pH was also calculated in milligram of chromium (VI) adsorbed per gram of adsorbent. As it is observed from the obtained information, higher adsorption was observed at pH = 2 which is 1.89 mg g^{-1} and minimum adsorption was observed at pH= 8 which is 1.75 mg g^{-1}.

4.2.3 Effect of Initial Concentration on Chromium (VI) & MB Adsorption

The Adsorption of chromium (VI) and MB ion on ACDWHL as a function of initial concentration was investigated by changing the initial concentration of chromium (VI) and MB ion from 2ppm to 10 ppm by keeping all parameters constant with adsorbent dose = 200 mg/50mL, stirring speed = 200 rpm, pH of 2 and 10, time = 90 min and the outcome are denoted in figure 17.

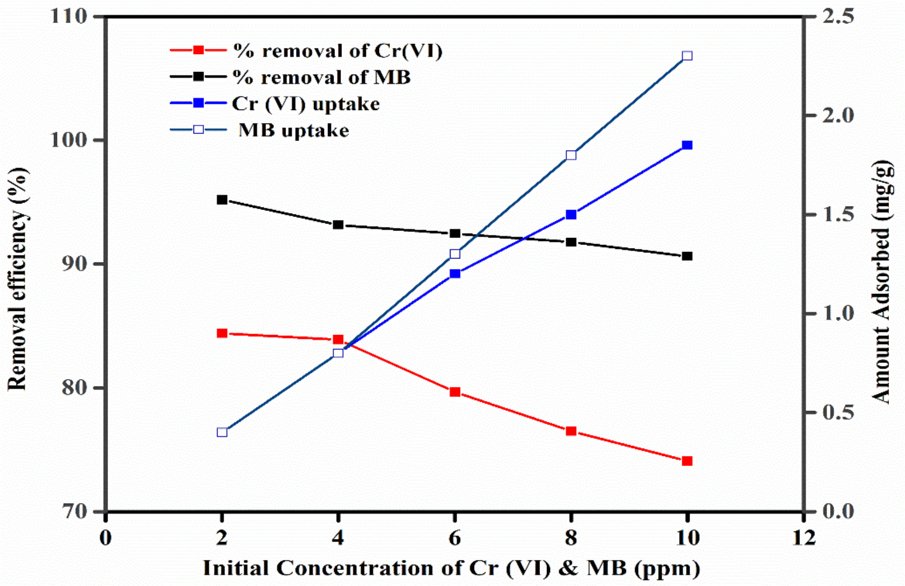

Figure 17: Effect of initial concentration on Cr (VI) & MB removal by ACDWHL.

It is noted that, with an increase in the initial concentration of chromium (VI) and MB ion from 2 ppm to 10 ppm, the percentage removal efficiency of chromium (VI) and MB ion was decreased from 84.4 to 74.08 % and 95.2 to 90.2%, respectively. Moreover, the amount of chromium (VI) and MB ion adsorbed on to the adsorbent increased from 0.4 to 1.85 mg g^{-1} & 0.4 to 2.3 mg g^{-1} with an increase in the initial concentration of chromium (VI) and MB ions from 2 ppm to 10 ppm. When the concentration of Cr (VI) and MB decreases, the presence of the active sites of the adsorbent would be increased. Therefore, the adsorption of chromium (VI) and MB ions was dependent on the initial concentration of chromium (VI) and MB ions, which was confirmed with the previously report [53]. The percentage removal of chromium (VI) and MB ion decreased as the concentration of chromium (VI) and MB ion increased in the solution [130]. This is due to fewer active sites being presented to adsorb chromium (VI) and MB ions when concentration was increased, because their sites saturate above a certain concentration. Therefore, at higher concentration of chromium (VI) and MB ion the percentage removal efficiency was decreased with corresponding initial chromium (VI) and MB concentration.

4.2.4 Effect of Adsorbent Dose on Cr (VI) and MB Adsorption

The effect of adsorbent dosage on the removal effectiveness of chromium (VI) and MB ion was examined over the range of adsorbent dose from 50, 100, 150, 200 and 250 mg, by keeping the optimum pH = 2 & 10, contact time= 90 min, stirring speed = 200 rpm and 10 ppm of chromium (VI) and MB concentration are constant. The outcome, shows that the percentage removal efficiency of chromium (VI) and MB was increased with an increasing in the adsorbent dose (figure 18). However, the adsorption capacity was decreased from 7.4 to 1.6 mg g^{-1} and 8.12 to 1.82 mg g^{-1}, respectively when the adsorbent dose increased from 50 mg – 250 mg.

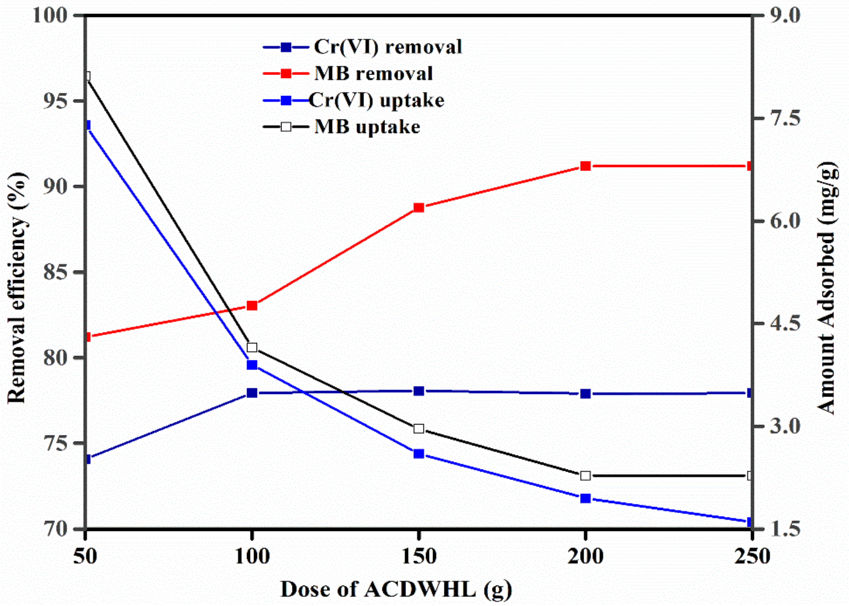

Figure 18: Effect of adsorbent dose on Cr (VI) & MB removal efficiency by ACDWHL.

Therefore, the percentage removal of ACDWHL was increased from 74.08 to 77.94 % & 81.20 to 91.20% when the adsorbent dose increased from 50 to 250 mg /50 mL. When 150 & 200 mg dose was used, the effectiveness of the removal percentage for chromium (VI) and MB reached at the adsorption equilibrium. When the ACDWHL dosage increased after the optimum value, the adsorption removal percentage was not increased for both chromium (VI) and MB. The surface area of the adsorbent dosage has a direct relationship with the active sites present in the ACDWHL. When the amount of the dose increased, the diffusion of chromium (VI) and MB molecules would be increased and it has not affected after the equilibrium was established.

From this investigation, it is confirmed that the percent removal efficiency was increased with increasing the dose of the adsorbent. However, the adsorption capacity in mg g^{-1} was decreased with increasing the adsorbent dose for chromium (VI) and MB. It is evident that the optimum amount of ACDWHL for supplementary adsorption experiments are 150 mg and 200 mg dosage and the removal efficiency of Cr (VI) and MB was selected as 77.94% & 91.2%, respectively.

4.2.5 Effect of Contact Time on Cr (VI) and MB Adsorption

To study the effect of contact time on the adsorption of Cr (VI) and MB, the pH =2 & 10, concentration =10 ppm, dose = 200 mg and stirring speed = 200 rpm were considered as constant and the experiment was conducted with varying contact time from 30, 60, 90, 120, 150 and 180 min. The result reveals that percentage removal of chromium (VI) and MB was increased with increasing in contact time. The percentage removal for chromium (VI) and MB was increased up to 120 and 90 min, respectively. However, when the contact time increased above 120 and 90 min, there was no change of the percent removal of chromium (VI) and MB. Moreover, the percentage removal of Cr (VI) and MB at 120 & 90 min was 74.97 & 91.07 %, respectively. Hence, the optimum contact time which was determined are 120 and 90 min, since after this point there was no change of the percent removal.

At the initial stages the high removal efficiency is due to the accessibility of large number of adsorption sites of chromium (VI) and MB is bound rapidly on adsorbent surface at a quick adsorption rate which saturated with time. The result shows that when the contact time increased, the adsorption of chromium (VI) and MB ion was increased (shown in figure 19). The adsorption capacity of chromium (VI) and MB from aqueous solution at different time interval was 1.75, 1.81, 1.84, 1.88, 1.863 & 1.86 mg g^{-1} and 2.03, 2.12, 2.277, 2.27, 2.269 & 2.274 mg g^{-1} as contact time increased from 30, 60, 90, 120, 150 & 180 min, respectively.

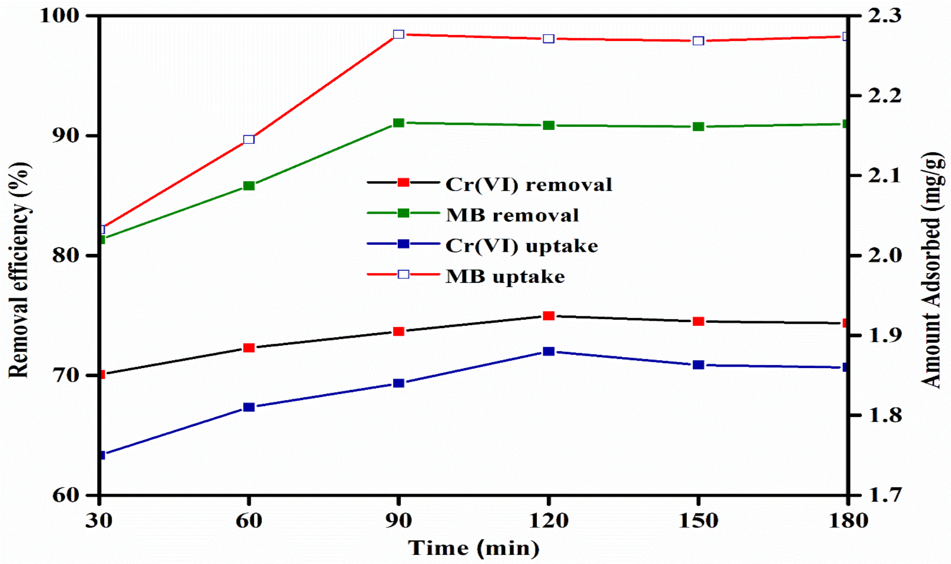

Figure 19: Effect of contact time on the removal of Cr (VI) & MB by using ACDWHL.

4.3 Adsorption Isotherm Study

Adsorption isotherm study shows that how the adsorbate interacts with the adsorbent and how an equilibrium is established between the adsorbed chromium (VI) and MB solution after surface adsorption. The models can be used to describe the relationship between the chromium (VI) and MB that needs to be adsorbed and the adsorbent [130]. Based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, type of coverage and possibility of interaction between adsorbate species. In this study, batch adsorption characteristics of Cr (VI) and MB removal with ACDWHL were conducted and the outcomes obtained from the experimentation were used to determine the better isotherm model that the adsorption process follows (Langmuir and Freundlich).

4.3.1 Langmuir Adsorption Isotherm

The isotherm model makes the qualitative assumption that after no additional adsorption has occurred, a monolayer of adsorbate has formed on the adsorbent's outer surface. This model states that there is no adsorbate transmigration on the surface after adsorption and that there is uniform energy of adsorption on the surface. The graph of $\frac{1}{\text{Ce}}$ vs $\frac{1}{\text{qe}}$ was plotted with varied equilibrium concentrations, as shown in figure 20 below, while the remaining parameters were unchanged. K_L

is the Langmuir constant and q_{max} is the maximum adsorption capacity (mg g^{-1}) which was calculated from the intercept and slope.

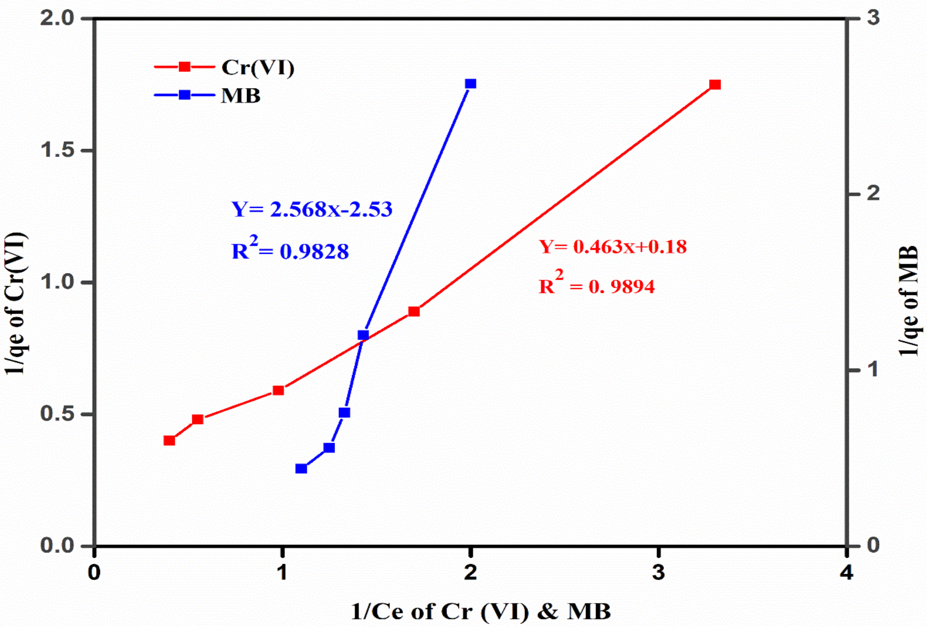

Figure 20: Langmuir adsorption isotherm model for Cr (VI) & MB.

Table 6 Langmuir adsorption isotherm parameters

Parameters	**Cr(VI)**	**MB**
q_{max}	0.463	2.568
K_L	0.18	2.53
R^2	0.9894	0.9828
R_L	0.7 to 0.36	0.17 to 0.04
Equations	$\frac{1}{qe} = 0.463 \frac{1}{Ce} + 0.18$	$\frac{1}{qe} = 2.568 \frac{1}{Ce} - 2.53$

The R_L (the separation factor) value was between 0 and 1 which indicating that the adsorption process for Cr (VI) and MB ion was acceptable by activated carbon (ACDWHL). The maximum adsorption capacity (q_{max}) determined by ACDWHL was 0.463 & 2.568 mg g^{-1} for Cr (VI) and MB, respectively. This implies that 0.463 & 2.568 mg of Cr (VI) and MB were absorbed per-gram of ACDWHL. The value of RL was from 0.7 to 0.36 & 0.17 to 0.04 for Cr (VI) and MB which indicates that adsorption of chromium (VI) and MB on ACDWHL was a favorable adsorption. The value of R^2 is 0.9894 for chromium (VI) which is greater than R^2 value of Freundlich adsorption isotherm. Therefore, the Langmuir adsorption isotherm model is well fit with the experimental results of chromium (VI). Moreover, the value of $R^2 = 0.9828$ for MB which is less than R^2 value of Freundlich adsorption isotherm. Because of this reason, the Langmuir adsorption isotherm model does not fit to describe the experimental result of MB.

4.3.2 Freundlich Adsorption Isotherm

The graph with *log* qe as the y-axis and *log* Ce as the x-axis was plotted in order to determine whether or not the Freundlich adsorption isotherm model fits to the experimental result. From linear equation, the value of Kf and $\frac{1}{n}$ was calculated and the Freundlich adsorption isotherm equation was established. The smaller $\frac{1}{n}$ values the greater the expected heterogeneity. If n , lies between one and ten or $\frac{1}{n}$ was less than one, it shows a favorable adsorption process [157].

The data in table 7 shows that the value of $\frac{1}{n}$ was 0.689 and 3.155, while n becomes 1.45 & 0.32, this approves that the adsorption of chromium (VI) and MB ion on ACDWHL was favorable and the value of R^2 are 0.9596 & 0.9978. From this conclude that MB adsorption data was fitted well to Freundlich adsorption isotherm model as compared to Langmuir. But for chromium (VI) the value of R^2 is 0.9596 which is less than the R^2 value of Langmuir adsorption isotherm. This confirms that the Freundlich adsorption isotherm model does not well fit to describe the experimental result of chromium (VI).

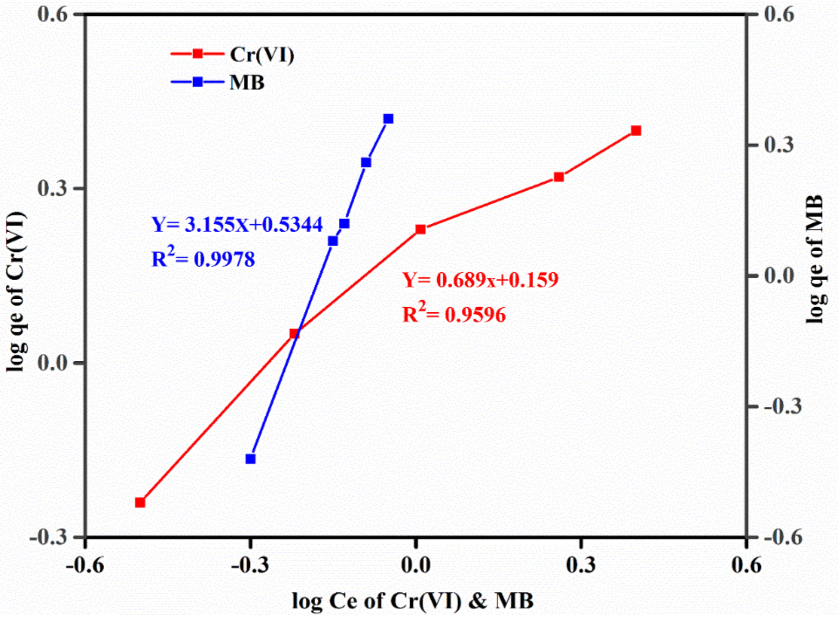

Figure 21: Freundlich adsorption isotherm model for chromium (VI) & MB.

Table 7 Freundlich adsorption isotherm parameters

Parameters	**Cr (VI)**	**MB**
N	1.45	0.32
$\frac{1}{n}$	0.689	3.155
R^2	0.9596	0.9978
K_f	1.44	3.42
Equation	*log* qe = 0.689 *log* Ce + 0.159	*log* qe = 3.155 *log* Ce + 0.5344

Generally, the isotherm parameters for each (Freundlich and Langmuir isotherm) respective models summarized in table 8. It shows almost higher correlation coefficient values, ($R^2 = 0.9596$ & 0.9978 for Cr (VI) and MB) were obtained for Freundlich isotherm model and ($R^2 = 0.9894$ & 0.9828 for chromium (VI) & MB) for Langmuir isotherm model. From those higher correlation coefficient values that is ($R^2 = 0.9894$ & $R^2 = 0.9978$ for Cr (VI) and MB respectively), which recommends that the adsorption of MB on the ACDWHL better fits with both models but, Freundlich model had a little higher R^2 value and it showed that the adsorption process could be due to multilayer adsorption manner on heterogeneous surface of the adsorbent. And also, the adsorption of Cr (VI) on the ACDWHL better fits with both models but, comparatively Langmuir isotherm model had a little higher R^2 value and it shows that the adsorption process could be due to monolayer adsorption on the homogeneous surface of the adsorbent.

Table 8 Adsorption isotherm parameters & coefficient of regression (R^2) for Cr (VI)& MB.

Isotherm Models & Parameter Values													
Langmuir								**Freundlich**					
q_{max}		**K_L**		**R_L**		**R^2**		**K_f**		**n_f**		**R^2**	
Cr	BM	Cr	MB	Cr	MB	Cr	MB	Cr	MB	Cr	MB	Cr	MB
0.5	2.6	0.2	2.5	0.7 to 0.4	0.2 to 0.04	0.9894	0.9828	1.4	3.4	1.5	0.3	0.9596	0.9978

4.4 Adsorption Kinetic study

Describes the chromium (VI) and MB removal rate as a function of equilibrium contact time. The linear pseudo first and second order kinetics were verified in order to study the kinetic model of the chromium (VI) and MB ion adsorption by ACDWHL and to investigate that which adsorption kinetics would fit with the experimental data. The kinetic models were acquired using the optimum dose = 150 mg and 200 mg, over a wide range of time 30 - 180 min with 10 ppm initial chromium (VI) and MB concentration.

4.4.1 Pseudo First Order Kinetic Model

The graph of *log* (qe–qt) vs t was plotted and its linearity was seen by taking the value of the correlation coefficient into consideration. The values of k_1 and qe were calculated from slope and intercept of the plot of *log* (qe–qt) vs t, respectively and table 9 summarizes the value of the kinetic parameters for first and second order. The pseudo first order plots of chromium (VI) and MB adsorption on ACDWHL for different time (30, 60, 90,120,150 & 180 min) are shown in figure 22. The value of R^2 for the pseudo first–order was, 0.5466 & 0.665 for chromium (VI) and MB, respectively which was lower as compared with the R^2 value of pseudo-second order. The lower R^2 value shows that adsorption of chromium (VI) and MB ion by ACDWHL does not follow pseudo first order kinetics.

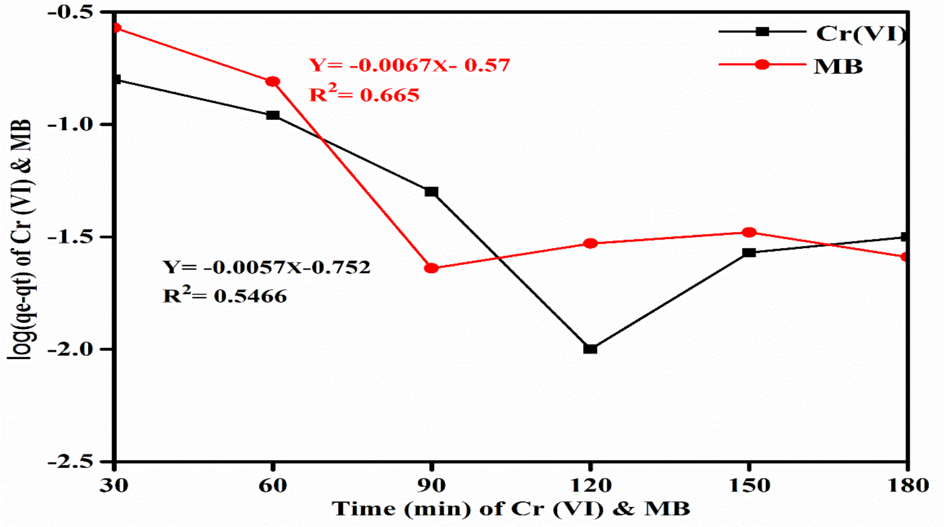

Figure 22: Pseudo first order kinetic curve for chromium (VI) & MB.

4.4.2 Pseudo Second Order Kinetics Model

To determine whether adsorption mechanism is determined by pseudo second order or not the graph of $\frac{t}{qt}$ vs t was plotted and its linearity was observed by considering correlation coefficient value. The values of qe and K_2 were calculated from slope and intercept of the plot of $\frac{t}{qt}$ vs t respectively. The pseudo second order plots of chromium (VI) and MB adsorption by ACDWHL for different time (30, 60, 90,120,150 & 180 min) are given in figure 23. The value of R^2 for the pseudo second-order was higher compared with the R^2 value of pseudo first order for both chromium (VI) and MB. Therefore, to describe the adsorption kinetics of chromium (VI) and MB ion by activated carbon, pseudo second-order adsorption model is more satisfactory, which shows that chemisorption is the rate limiting step. The calculated and experimental adsorption capacities are very close. This indicates that the validation and application of pseudo second order in the adsorption process was favorable [130].

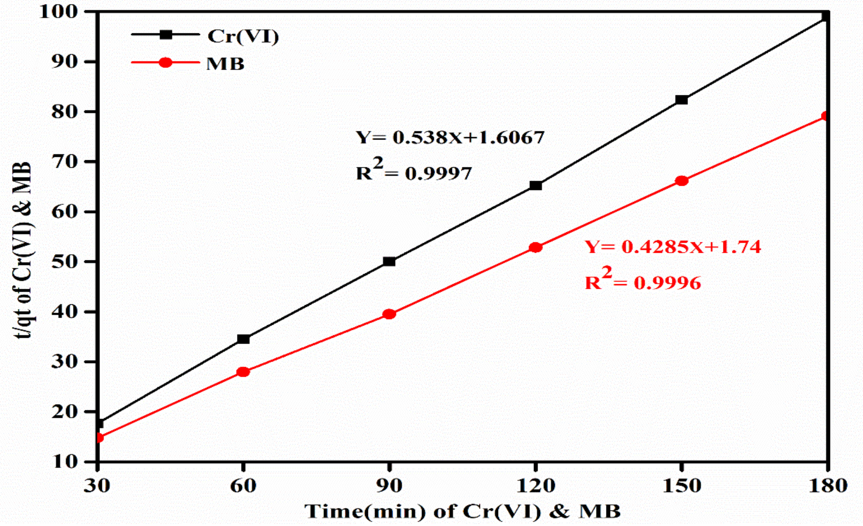

Figure 23: Pseudo second order kinetic curve for chromium (VI) & MB.

Table 9 Adsorption Kinetic parameters for chromium (VI) & MB

Kinetic Model	**Parameters with respective value**							
	K_1 & K_2		qe(cal)		qe (exp)		R^2	
	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
1st order	1.3×10^{-2}	1.54×10^{-2}	0.177	0.27	1.85	2.3	0.5466	0.665
2ndorder	1.8×10^{-1}	1.08×10^{-1}	1.86	2.33	1.85	2.3	0.9997	0.9996

4.5 Application of ACDWHL for Tannery and Textile Wastewater Treatment

The sewage samples were taken from pre-treatment and post-treatment site outlet of leather and textile industry so called Bahir Dar leather and textile production. The concentrations of chromium (VI) and MB in the real water samples taken from pre-treatment and post-treatment site was higher than the permissible level of WHO standards (0.05 ppm for chromium (VI) as shown in table 10. The efficiency of the ACDWHL to remove Chromium (VI) and MB has been tested with real wastewater sample at the pre-treatment and post-treatment by keeping all the parameters constant with an optimum contact time =120 & 90 min, dose = 150 mg & 200 mg, pH =2 & 10, for chromium (VI) and MB, respectively. The concentration of chromium (VI) and MB in the real sample in the pretreatment was 4.465 ± 0.15 ppm & 10.306 ± 0.16 ppm and also in the post-treatment the concentration was reduced to 3.16 ± 0.25 & 1.52 ± 0.05 ppm after adsorption at pH

2 and 10, respectively (shown in table 10). The maximum percentage removal efficiency was 58.76% & 67.03% at pH 2 & 10 for chromium (VI) and MB respectively and the removal effectiveness decreased when compared to aqueous solution prepared in laboratory. This may be due to the existence of other metals and different matrix in tannery and textile sewage which competed with chromium (VI) and MB to adsorb on ACDWHL. This may be due the interfering ions such as anions namely SO_4^{2-}, CO_3^{2-}, NO_3^{-}, Cl^{-} and PO_4^{3-} and cations, such as Ca^{2+}, Mg^{2+}, Cu^{2+} and Fe^{2+} [53].

Table 10 Removal of Cr (VI) & MB from real water at optimized condition.

Type of sample	**BTWW**	**ATWW**	**BTA WW**	**ATAWW**	**%Removal**		**Adsorption Capacity**	
					BTA WW	ATA WW	BTA WW	ATA WW
TWW	4.47 ±0.15	3.16±0.25	2.082±0.15	1.3±0.2	53.4	58.76	0.8	0.62
TXWW	10.3±0.16	1.52±0.05	6.2±0.13	0.5±0.02	40.4	67.03	1.03.	0.26

4.6 Comparison of the Adsorbent with other Adsorbents

The adsorption capacity and the percent removal for chromium (VI) and MB ion for the as-prepared material has been compared with the previously work and shown in table 11. The percentage removal of chromium (VI) and MB, under this study were better as compared with most literature values. low cost and easily available adsorbent materials are selected for comparison.

Table 11 Comparison of the percentage removal of d/f adsorbents for Cr (VI) & MB.

For chromium (VI) Comparison			
Adsorbents	Adsorption capacity (mg/g)	% Removal	Reference
Oak wood charcoal	30.1	75	[158]
Sunflower stem waste	4.81	76.5	[159]
Red pine sawdust	8.3	87.7	[160]
Waste newspaper	5.88	64	[24]
Ragi husk	__	68.6	[161]
Water hyacinth leaf	7.4	84.4	This work
For MB Comparison			
Barley bran	63.2	80	[162]
Oil palm wastes	24	78.58	[30]
Enset midrib leaf	3.55	80	[162]
Kola nitida	0.7871	94	[163]
Tea waste	13.15	90	[164]
Water hyacinth leaf	8.12	95.2	This work

4.7 The Adsorption Mechanisms of Chromium (VI) & MB

Interaction between Cr(VI)-Adsorbent: Solution pH decides the ionic state of the adsorbate and active functional groups of the adsorbent[165].There can be four possible mechanisms for the adsorption of Cr(VI) onto ACDWHL, based on the outcomes of the pHpzc (5.4) and verified in fig 25 . Firstly, adsorption mechanism (pH solution < pHpzc), an increase in the concentration of H^+ protonates the surface of ACDWHL which becomes positively charged surface and also there is a negatively charged Cr (VI) species ($HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}). Due to the presence of the electrostatic attraction between the two charges, which would contribute as a main driving force behind the adsorption process. These oxygen-containing functional groups (–OH, COOH, NH_2 and C−O) in ACDWHL, as observed in the FTIR analysis played a significant role the in electrostatic attraction. Secondly, when pH solution > pHpzc, implies that the surface becomes negative charge which is replaced by Cr (VI) anionic species through ion exchange. Thirdly, at pH solution > pHpzc, ACDWHL surface becomes negatively charged that counter to reduced adsorption process exhibiting electrostatic repulsion [166]. Fourthly, there is a possibility that physical exchange of ions between Cr species and ACDWHL surface and the adsorption process would be a physical.

Interaction between MB dye-Adsorbent: The mechanism behind the adsorption of MB onto ACDWHL has been indicated in fig 24. Firstly, electrostatic interaction played a major role in the uptake of MB with change in solution pH. The oxygen-containing functional groups (–OH, NH_2 and COOH) confirmed by the FTIR analysis on the surface of ACDWHL have a vital role for MB adsorption through electrostatic interaction. Secondly due to the existence of hydrogen bonding (OH, $-NH_2$ and COOH groups on the surface ACDWHL and with nitrogen on MB dye) the presence of this bond enhanced the adsorption of organic pollutant MB through interaction. Thirdly there is a possibility that physical exchange of ions between MB and ACDWHL surface may switch the adsorption process to physical adsorption (simply pore filling). Fourthly, there was electro statical repulsion and ion exchange (pH solution < pHpzc), due to positively charged MB and ACDWHL surface. Generally, isotherm modeling of Cr (VI) and MB adsorption process on ACDWHL showed chemisorption as a predominant process in the adsorption process. Similarly, intra-particle diffusion (kinetic model) confirmed the rate-limiting step for adsorption of adsorbate onto adsorbent was controlled by film diffusion, establishing a link for chemisorption of Cr(VI) and MB on the active sites of ACDWHL[165].

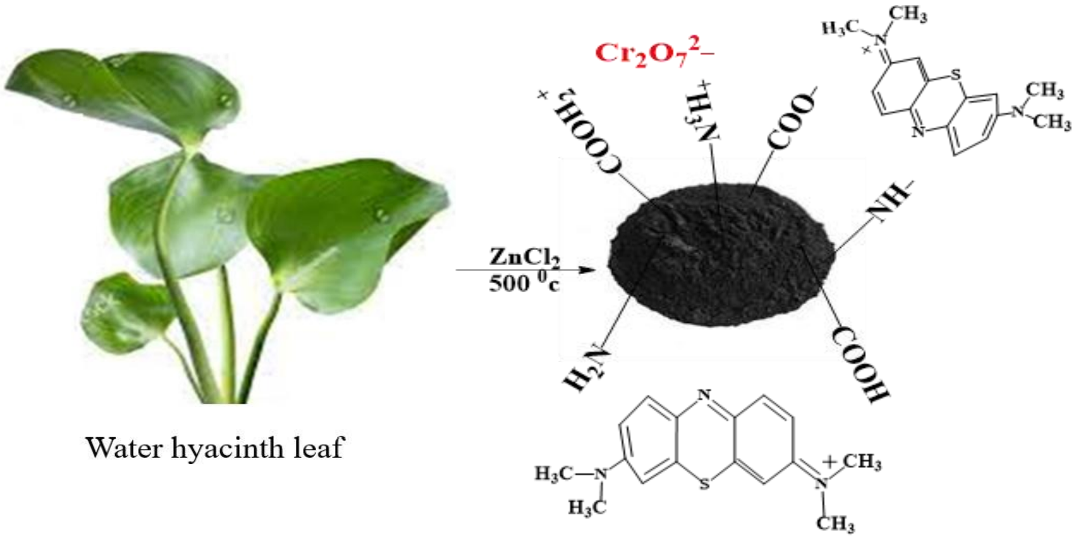

Figure 24: Proposed reaction mechanism b/n ACDWHL with Cr(VI) and MB.

5 CONCLUSION & RECOMMENDATION

5.1 Conclusion

This study has investigated the preparation and characterization of ACDWHL from water hyacinth leaf by chemical activation using $ZnCl_2$ and its application for Cr (VI) and MB removal. The ACDWHL were characterized through proximate analysis, XRD, FTIR, and BET. The BET surface area of ACDWHL was found to be 616.387 m^2/g. The results of batch experiments showed that adsorption of Cr (VI) and MB by ACDWHL depends on various parameters such as pH, dosage, contact time and initial concentration of Cr (VI) and MB. The optimum pH was = 2 & 10, adsorbent dose = 150 & 200 mg, contact time = 120 & 90 min and initial concentrations of 2 ppm for Cr (VI) and MB were observed, respectively. The maximum uptake (mg g−1) of the adsorbent obtained for Cr (VI) and MB was found to be 7.4 and 8.12 mg g−1 as well as the maximum percentage removals of Cr (VI) and MB obtained was 84.4 and 95.2%. However, the maximum percentage removal efficiency of real sample was 58.76 and 67.03% at pH 2 and 10 consecutively for Cr (VI) and MB this indicates the real wastewater sample the removal efficiency decreased when compared to aqueous solution prepared in laboratory. The Cr (VI) adsorption followed Langmuir isotherm, whereas MB followed Freundlich isotherm. A pseudo-second order kinetic model fits for both Cr (VI) and MB. Generally, the ACDWHL was found to be an effective bio-adsorbent for the removal of Cr (VI) and MB from tannery & textile wastewater. The result shows that the ACDWHL has high capacity and efficiency in removing Cr (VI) and MB ion in wastewater/synthetic water. Hence, the prepared material would be employed for the adsorption of Cr (VI) and methylene blue in wastewater like, tannery& textile, which was environmentally benign.

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5.2 Recommendation

Activated carbon prepared from water hyacinth leaf by chemical activation using $ZnCl_2$ had been shown to have the potential to remove Cr (VI) and MB ions from aqueous solution/industrial effluents. The following studies and ideas could be recommending to other researchers and the government.

- ✓ Real sample or industrial effluents may contain many an interfering ion this may be due the interfering ions such as anions namely SO_4^{2-}, CO_3^{2-}, NO_3^{-}, Cl^{-} and PO_4^{3-} and cations, namely Ca^{2+}, Mg^{2+}, Cu^{2+} and Fe^{2+} such ions that compete with Cr (VI) and MB for adsorption. Therefore, the effect of interfering ions should be investigated.
- ✓ Investigate the reusability of the adsorbent.
- ✓ In this thesis, the water hyacinth leaf was used to make the activated carbon, however further study needed to produce the activated carbon from its root.
- ✓ The activated carbon prepared from water hyacinth leaf must be applied for the removal of other heavy metals and dyes.
- ✓ The spread of water hyacinth in Abay River increased from time to time, therefore, it is now recommended that the government should encourage this kind of research works by recommending it to the users and by adopted in industrial scale.

6 REFERENCE

1. Madhav, S.,Ahamad, A.,Singh, A. K.,Kushawaha, J.,Chauhan, J. S.,Sharma, S.,Singh, P., (2020). Water pollutants: sources and impact on the environment and human health. *Sensors in Water Pollutants Monitoring: Role of Material*, 43-62.

2. Sharma, S.,Bhattacharya, A., (2017). Drinking water contamination and treatment techniques. *Applied water science***, 7** (3), 1043-1067.

3. Mia, M.,Sayid, A.,Ahmad, F.,Rahman, M., (2020). An overview of chromium removal techniques from tannery effluent. *Applied Water Science***, 10** (9), 1-22.

4. Baquero, G.,Sorolla, S.,Cuadros, R.,Ollé, L.,Bacardit, A., (2021). Analysis of the environmental impacts of waterproofing versus conventional vegetable tanning process-A life cycle analysis study. *Journal of Cleaner Production***, 325**, 129344.

5. Onem, E.,Yorgancioglu, A.,Karavana, H. A.,Yilmaz, O., (2017). Comparison of different tanning agents on the stabilization of collagen via differential scanning calorimetry. *Journal of Thermal Analysis and Calorimetry***, 129** (1), 615-622.

6. Lofrano, G.,Meriç, S.,Zengin, G. E.,Orhon, D., (2013). Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. *Science of the Total Environment***, 461**, 265-281.

7. Saxena, G.,Chandra, R.,Bharagava, R. N., (2016). Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. *Reviews of Environmental Contamination and Toxicology Volume 240*, 31-69.

8. Nigam, M.,Rajoriya, S.,Singh, S. R.,Kumar, P., (2019). Adsorption of Cr (VI) ion from tannery wastewater on tea waste: kinetics, equilibrium and thermodynamics studies. *Journal of Environmental Chemical Engineering***, 7** (3), 103188.

9. Ishchenko, V., (2018). Environment contamination with heavy metals contained in waste. *Environmental Problems. Vol. 3, No. 1: 21-24.*

10. Focardi, S.,Pepi, M.,Focardi, S. E., (2013). Microbial reduction of hexavalent chromium as a mechanism of detoxification and possible bioremediation applications. *Biodegradation-life of science*, 321-347.

11. Udiba, U.,Odey, M.,Lydia, E., (2017). Pollution potential of effluent from challawa industrial layout and its influence on the water quality of River Challawa, Kano, Nigeria.

12. Martín, A.,Arias, J.,López, J.,Santos, L.,Venegas, C.,Duarte, M.,Ortíz-Ardila, A.,de Parra, N.,Campos, C.,Zambrano, C. C., (2020). Evaluation of the effect of gold mining on the water quality in Monterrey, Bolívar (Colombia). *Water***, 12** (9), 2523.

13. Rather, L. J.,Akhter, S.,Hassan, Q. P.,Mohammad, F., (2017). Chemistry of plant dyes: Applications and environmental implications of dyeing processes. *Current Environmental Engineering***, 4** (2), 103-120.

14. Laysandra, L.,Sari, M. W. M. K.,Soetaredjo, F. E.,Foe, K.,Putro, J. N.,Kurniawan, A.,Ju, Y.-H.,Ismadji, S., (2017). Adsorption and photocatalytic performance of bentonite-titanium dioxide composites for methylene blue and rhodamine B decoloration. *Heliyon***, 3** (12), e00488.

15. Kuang, Y.,Zhang, X.,Zhou, S., (2020). Adsorption of methylene blue in water onto activated carbon by surfactant modification. *Water***, 12** (2), 587.

16. Gupta, V.,Pathania, D.,Singh, P.,Kumar, A.,Rathore, B., (2014). Adsorptional removal of methylene blue by guar gum–cerium (IV) tungstate hybrid cationic exchanger. *Carbohydrate polymers***, 101**, 684-691.

17. Oncel, M.,Muhcu, A.,Demirbas, E.,Kobya, M., (2013). A comparative study of chemical precipitation and electrocoagulation for treatment of coal acid drainage wastewater. *Journal of Environmental Chemical Engineering***, 1** (4), 989-995.

18. Palakkeel Veetil, D.,Mercier, G.,Blais, J.-F.,Chartier, M.,Tran, L. H., (2013). Simultaneous removal of Cu and PAHs from dredged sediments using flotation. *Journal of Soils and Sediments***,** **13** (8), 1502-1514.

19. Caprarescu, S.,Miron, A. R.,Purcar, V.,Radu, A. L.,Sarbu, A.,Ianchis, R.,Erbasu, D. I., (2017). Commercial gooseberry buds extract containing membrane for removal of methylene blue dye from synthetic wastewaters. *Rev Chim (Bucharest)***,** **68**, 1757-1762.

20. Ali, I.,Asim, M.,Khan, T. A., (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. *Journal of environmental management***,** **113**, 170-183.

21. Pakade, V. E.,Tavengwa, N. T.,Madikizela, L. M., (2019). Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods. *RSC advances***,** **9** (45), 26142-26164.

22. Parlayici, Ş.,Pehlivan, E., (2019). Comparative study of Cr (VI) removal by bio-waste adsorbents: equilibrium, kinetics, and thermodynamic. *Journal of Analytical Science and Technology***,** **10** (1), 1-8.

23. Khan, T.,Isa, M. H.,Mustafa, M. R. U.,Yeek-Chia, H.,Baloo, L.,Abd Manan, T. S. B.,Saeed, M. O., (2016). Cr (VI) adsorption from aqueous solution by an agricultural waste based carbon. *RSC advances***,** **6** (61), 56365-56374.

24. Dehghani, M. H.,Sanaei, D.,Ali, I.,Bhatnagar, A., (2016). Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: kinetic modeling and isotherm studies. *Journal of molecular liquids***,** **215**, 671-679.

25. Sharma, P. K.,Ayub, S.,Tripathi, C. N., (2016). Isotherms describing physical adsorption of Cr (VI) from aqueous solution using various agricultural wastes as adsorbents. *Cogent Engineering***,** **3** (1), 1186857.

26. Garg, K.,Rawat, P.,Prasad, B., (2015). Removal of Cr (VI) and COD from electroplating wastewater by corncob based activated carbon. *Int J Water Wastewater Treat***,** **1**.

27. Zazycki, M. A.,Godinho, M.,Perondi, D.,Foletto, E. L.,Collazzo, G. C.,Dotto, G. L., (2018). New biochar from pecan nutshells as an alternative adsorbent for removing reactive red 141 from aqueous solutions. *Journal of Cleaner Production***, 171**, 57-65.

28. Khan, T. A.,Singh, V. V., (2010). Removal of cadmium (II), lead (II), and chromium (VI) ions from aqueous solution using clay. *Toxicological and environ chemistry***, 92** (8), 1435-1446.

29. Mahapatra, U.,Chatterjee, A.,Das, C.,Manna, A. K., (2021). Adsorptive removal of hexavalent chromium and methylene blue from simulated solution by activated carbon synthesized from natural rubber industry biosludge. *Environmental Technology & Innovation***, 22**, 101427.

30. Baloo, L.,Isa, M. H.,Sapari, N. B.,Jagaba, A. H.,Wei, L. J.,Yavari, S.,Razali, R.,Vasu, R., (2021). Adsorptive removal of methylene blue and acid orange 10 dyes from aqueous solutions using oil palm wastes-derived activated carbons. *Alexandria Engineering Journal***, 60** (6), 5611-5629.

31. Lellis, B.,Fávaro-Polonio, C. Z.,Pamphile, J. A.,Polonio, J. C., (2019). Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnology Research and Innovation***, 3** (2), 275-290.

32. Abdel-Raouf, M.,Abdul-Raheim, A., (2017). Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: Page 2 of 13 Volume 5,. *Mercury***, 8**, 15-19.

33. Majeed, M. R.,Muhammed, A. S.,Rasheed, K. A., (2014). The removal of Zinc, Chromium and Nickel from industrial waste water using Rice husk. *Iraqi Journal of Science***, 55** (2A), 411-418.

34. Renge, V.,Khedkar, S.,Pande, S. V., (2012). Removal of heavy metals from wastewater using low cost adsorbents: a review. *Sci. Revs. Chem. Commun***, 2** (4), 580-584.

35. Et, A.,Shahmohammadi-Kalalagh, S., (2011). Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite. *Caspian Journal of Environmental Sciences***, 9** (2), 243-255.

36. Gavrilescu, M.,Demnerová, K.,Aamand, J.,Agathos, S.,Fava, F., (2015). Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. *New biotechnology***, 32** (1), 147-156.

37. Bánfalvi, G., Heavy metals, trace elements and their cellular effects. In *Cellular effects of heavy metals*, Springer: 2011; pp 3-28.

38. Masindi, V.,Muedi, K. L., (2018). Environmental contamination by heavy metals. *Heavy metals***,** **10**, 115-132.

39. Younas, F.,Mustafa, A.,Farooqi, Z. U. R.,Wang, X.,Younas, S.,Mohy-Ud-Din, W.,Ashir Hameed, M.,Mohsin Abrar, M.,Maitlo, A. A.,Noreen, S., (2021). Current and emerging adsorbent technologies for wastewater treatment: trends, limitations, and environmental implications. *Water***,** **13** (2), 215.

40. Abas, S.,Ismail, M.,Kamal, M.,Izhar, S., Adsorption process of heavy metals by low-cost adsorbent: a review. World Appl Sci J 28: 1518–1530. 2013.

41. Mohod, C. V.,Dhote, J., (2013). Review of heavy metals in drinking water and their effect on human health. *International Journal of Innovative Research in Science, Engineering and Technology***,** **2** (7), 2992-2996.

42. Yesmeen, R.,Zakir, H.,Alam, M.,Mallick, S., (2018). Heavy metal and major ionic contamination level in effluents, surface and groundwater of an urban industrialised city: A case study of Rangpur city, Bangladesh. *Asian J Chem Sci***,** **5** (1), 1-16.

43. Pereira, S. C.,Oliveira, P. F.,Oliveira, S. R.,Pereira, M. d. L.,Alves, M. G., (2021). Impact of environmental and lifestyle use of chromium on male fertility: focus on antioxidant activity and oxidative stress. *Antioxidants***,** **10** (9), 1365.

44. Ghiloufi, I.,Khezami, L.,El Mir, L., (2015). Nanoporous activated carbon for fast uptake of heavy metals from aqueous solution. *Desalination and Water Treatment***,** **55** (4), 935-944.

45. Sundaram, S.,Raghavan, P., *Chromium-VI reagents: synthetic applications*. Springer Science & Business Media: 2011.

46. Chowdhury, M. Y., (2017). Isolation and characterization of chromium resistant bacteria from marine soil.

47. Masud, K. N. A., (2017). Isolation and characterization of chromium resistant bacteria from sea bed soil.

48. Adeiga, O. I., *Macadamia Nutshell Decorated Polyaniline Nanocomposites (Mns-Pani) for the Removal of Cr (Vi) and Its Re-Use for Photocatalytic Degradation*. *University of Johannesburg (South Africa)*: 2021.

49. Oliveira, H., (2012). Chromium as an environmental pollutant: insights on induced plant toxicity. *Journal of Botany*.

50. Shi, J.,McGill, W. B.,Chen, N.,Rutherford, P. M.,Whitcombe, T. W.,Zhang, W., (2020). Formation and immobilization of Cr (VI) species in long-term tannery waste contaminated soils. *Environmental Science & Technology***, 54** (12), 7226-7235.

51. Gholipour, M.,Hashemipour, H.,Mollashahi, M., (2011). Hexavalent chromium removal from aqueous solution via adsorption on granular activated carbon: adsorption, desorption, modeling and simulation studies. *J. Eng. Appl. Sci***, 6** (9), 10-18.

52. Mishra, S.,Bharagava, R. N., (2016). Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies. *Journal of Environmental Science and Health, Part C***, 34** (1), 1-32.

53. Ravulapalli, S.,Kunta, R., (2018). Enhanced removal of chromium (VI) from wastewater using active carbon derived from Lantana camara plant as adsorbent. *Water Science and Technology***, 78** (6), 1377-1389.

54. Brose, D. A.,James, B. R., (2013). Hexavalent chromium reduction by tartaric acid and isopropyl alcohol in Mid-Atlantic soils and the role of Mn (III, IV)(hydr) oxides. *Environmental science & technology***, 47** (22), 12985-12991.

55. Khulbe, K.,Matsuura, T., (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. *Applied water science***, 8** (1), 1-30.

56. Vishnu, D.,Dhandapani, B.,Authilingam, S.,Sivakumar, S. V., (2022). A comprehensive review of effective adsorbents used for the removal of dyes from wastewater. *Current Analytical Chemistry*, **18** (3), 255-268.

57. Yagub, M. T.,Sen, T. K.,Afroze, S.,Ang, H. M., (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science*, **209**, 172-184.

58. Gueret, R.,Poulard, L.,Oshinowo, M.,Chauvin, J.,Dahmane, M.,Dupeyre, G.,Lainé, P. P.,Fortage, J.,Collomb, M.-N., (2018). Challenging the [Ru (bpy) 3] 2+ photosensitizer with a triazatriangulenium robust organic dye for visible-light-driven hydrogen production in water. *Acs Catalysis*, **8** (5), 3792-3802.

59. Benkhaya, S.,M'rabet, S.,El Harfi, A., (2020). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications*, **115**, 107891.

60. Shah, M. P., Bioremediation of azo dye. In *Microbial wastewater treatment,* Elsevier: 2019; pp 103-126.

61. Önal, E. S.,Yatkin, T.,Ergüt, M.,Özer, A., (2017). Green synthesis of iron nanoparticles by aqueous extract of Eriobotrya japonica leaves as a heterogeneous fenton-like catalyst: degradation of basic red 46. *International Journal of Chemical Engineering and Applications*, **8** (5), 327-333.

62. Bilińska, L.,Gmurek, M.,Ledakowicz, S., (2016). Comparison between industrial and simulated textile wastewater treatment by AOPs–Biodegradability, toxicity and cost assessment. *Chemical Engineering Journal*, **306**, 550-559.

63. Fatiha, M.,Belkacem, B., (2016). Adsorption of methylene blue from aqueous solutions using natural clay. *J. Mater. Environ. Sci*, **7** (1), 285-292.

64. Wong, Y.,Senan, M.,Atiqah, N., (2013). Removal of methylene blue and malachite green dye using different form of coconut fibre as absorbent. *Journal of Basic & Applied Sciences*, **9**, 172.

65. Quan, X.,Luo, D.,Wu, J.,Li, R.,Cheng, W., (2017). Ozonation of acid red 18 wastewater using O3/Ca (OH) 2 system in a micro bubble gas-liquid reactor. *Journal of Environmental Chemical Engineering*, **5** (1), 283-291.

66. Sharma, J.,Sharma, S.,Soni, V., (2021). Classification and impact of synthetic textile dyes on Aquatic Flora: A review. *Regional Studies in Marine Science*, **45**, 101802.

67. Dawood, S. A. Synthesis and Characterization of Biomass and Clay Mineral Based Adsorbents for the Removal of Cationic Dye and Metal Ion from Wastewater by Adsorption. Curtin University, 2018.

68. Shakoor, S.,Nasar, A., (2016). Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent. *Journal of the Taiwan Institute of Chemical Engineers*, **66**, 154-163.

69. Barakat, M., (2011). New trends in removing heavy metals from industrial wastewater. *Arabian journal of chemistry*, **4** (4), 361-377.

70. Zheng, H.,Zhu, G.,Jiang, S.,Tshukudu, T.,Xiang, X.,Zhang, P.,He, Q., (2011). Investigations of coagulation–flocculation process by performance optimization, model prediction and fractal structure of flocs. *Desalination*, **269** (1-3), 148-156.

71. Liu, L.,Wang, L.,Yin, L.,Song, W.,Yu, J.,Liu, Y., (2014). Effects of different solvents on the surface acidic oxygen-containing functional groups on Xanthoceras sorbifolia shell. *BioResources*, **9** (2), 2248-2258.

72. Wang, Z.,Feng, Y.,Hao, X.,Huang, W.,Feng, X., (2014). A novel potential-responsive ion exchange film system for heavy metal removal. *Journal of Materials Chemistry A*, **2** (26), 10263-10272.

73. Keng, P.-S.,Lee, S.-L.,Ha, S.-T.,Hung, Y.-T.,Ong, S.-T., (2014). Removal of hazardous heavy metals from aqueous environment by low-cost adsorption materials. *Environmental Chemistry Letters*, **12** (1), 15-25.

74. Gunatilake, S., (2015). Methods of removing heavy metals from industrial wastewater. *Methods*, **1** (1), 14.

75. Wang, L. K.,Vaccari, D. A.,Li, Y.,Shammas, N. K., Chemical precipitation. In *Physicochemical treatment processes*, Springer: 2005; pp 141-197.

76. Malik, D.,Jain, C.,Yadav, A. K., (2017). Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review. *Applied water science*, **7** (5), 2113-2136.

77. Arbabi, M.,Golshani, N., (2016). Removal of copper ions Cu (II) from industrial wastewater: A review of removal methods. *International Journal of Epidemiologic Research*, **3** (3), 283-293.

78. Mukhopadhyay, K.,Chakrabarti, S. In *Heavy metal memediation in water treatmet systems : revisiting some useful applications and processes* Disaster, risk and vulnerability conference, 2014; p 184.

79. Shammas, N. K.,Pouet, M.-F.,Grasmick, A., Wastewater treatment by electrocoagulation–flotation. In *Flotation technology*, Springer: 2010; pp 199-220.

80. Deliyanni, E. A.,Kyzas, G. Z.,Matis, K. A., (2017). Various flotation techniques for metal ions removal. *Journal of Molecular Liquids*, **225**, 260-264.

81. Kyzas, G. Z.,Matis, K. A., (2018). Flotation in water and wastewater treatment. *Processes*, **6** (8), 116.

82. Garba, M. D.,Usman, M.,Mazumder, M. A. J.,Al-Ahmed, A., (2019). Complexing agents for metal removal using ultrafiltration membranes: a review. *Environmental Chemistry Letters*, **17** (3), 1195-1208.

83. Shrestha, R.,Ban, S.,Devkota, S.,Sharma, S.,Joshi, R.,Tiwari, A. P.,Kim, H. Y.,Joshi, M. K., (2021). Technological trends in heavy metals removal from industrial wastewater: A review. *Journal of Environmental Chemical Engineering*, **9** (4), 105688.

84. Tripathi, A.,Ranjan, M. R., (2015). Heavy metal removal from wastewater using low cost adsorbents. *J Bioremed Biodeg***, 6** (6), 315.

85. Afroze, S.,Sen, T. K., (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water, Air, & Soil Pollution***, 229** (7), 1-50.

86. Kyzas, G. Z.,Kostoglou, M., (2014). Green adsorbents for wastewaters: a critical review. *Materials***, 7** (1), 333-364.

87. Soberman, M. Design, Characterization, and Performance of Composite Electrospun Nanofiber Membrane Adsorption Systems for the Removal of Pharmaceutical and Personal Care Products from Water. University of Toronto (Canada), 2021.

88. Lewoyehu, M., (2021). Comprehensive review on synthesis and application of activated carbon from agricultural residues for the remediation of venomous pollutants in wastewater. *Journal of Analytical and Applied Pyrolysis***, 159**, 105279.

89. Girish, C.,Murty, V. R., (2012). Adsorption of phenol from wastewater using locally available adsorbents. *Journal of Environmental Research and development***, 6** (3A), 763-772.

90. Elsayed, A.,Mahmoud, S.,Al-Dadah, R.,Bowen, J.,Kaialy, W., (2014). Experimental and numerical investigation of the effect of pellet size on the adsorption characteristics of activated carbon/ethanol. *Energy Procedia***, 61**, 2327-2330.

91. Mukherjee, S. S.,Gangradey, R.,Nayak, P.,Panchal, P.,Agarwal, J.,Stephen, M.,Mishra, J. S.,Rana, C., (2018). Study on forms of activated carbon related to application in CryosorptionCryopump. *Materials Today: Proceedings***, 5** (2), 6195-6202.

92. Coman, V.,Robotin, B.,Ilea, P., (2013). Nickel recovery/removal from industrial wastes: A review. *Resources, Conservation and Recycling***, 73**, 229-238.

93. Dhir, B., (2014). Potential of biological materials for removing heavy metals from wastewater. *Environmental science and pollution research***, 21** (3), 1614-1627.

94. Madsen, J. D.,Morgan, C. M., (2021). Water temperature controls the growth of waterhyacinth and South American sponge plant. *J. Aquat. Plant Manag*, 28-32.

95. Zhang, Q.,Weng, C.,Huang, H.,Achal, V.,Wang, D., (2016). Optimization of bioethanol production using whole plant of water hyacinth as substrate in simultaneous saccharification and fermentation process. *Frontiers in Microbiology***, 6**, 1411.

96. Sagar, C. V.,Kumari, N. A., (2013). Sustainable biofuel production from water Hyacinth (Eicchornia crassipes). *Int J Eng Trends Technol***, 4** (10), 4454-4458.

97. Akter, M.,Bhattacharjee, M.,Dhar, A. K.,Rahman, F. B. A.,Haque, S.,Rashid, T. U.,Kabir, S., (2021). Cellulose-based hydrogels for wastewater treatment: A concise review. *Gels***, 7** (1), 30.

98. Degaga, A. H., (2018). Water Hyacinth (Eichhornia crassipes) Biology and its Impacts on Ecosystem, Biodiversity, Economy and Human Wellbeing. *Journal of Life Science and Biomedicine***, 8**, 94-100.

99. Bhagavathi Pushpa, T.,Vijayaraghavan, J.,Vijayaraghavan, K.,Jegan, J., (2016). Utilization of Effective Microorganisms based water hyacinth compost as biosorbent for the removal of basic dyes. *Desalination and water treatment***, 57** (51), 24368-24377.

100. Feng, W.,Xiao, K.,Zhou, W.,Zhu, D.,Zhou, Y.,Yuan, Y.,Xiao, N.,Wan, X.,Hua, Y.,Zhao, J., (2017). Analysis of utilization technologies for Eichhornia crassipes biomass harvested after restoration of wastewater. *Bioresource technology***, 223**, 287-295.

101. Smolyakov, B. S., (2012). Uptake of Zn, Cu, Pb, and Cd by water hyacinth in the initial stage of water system remediation. *Applied geochemistry***, 27** (6), 1214-1219.

102. Heidarinejad, Z.,Dehghani, M. H.,Heidari, M.,Javedan, G.,Ali, I.,Sillanpää, M., (2020). Methods for preparation and activation of activated carbon: a review. *Environmental Chemistry Letters***, 18** (2), 393-415.

103. Byamba-Ochir, N.,Shim, W. G.,Balathanigaimani, M.,Moon, H., (2016). Highly porous activated carbons prepared from carbon rich Mongolian anthracite by direct NaOH activation. *Applied Surface Science***, 379**, 331-337.

104. Reza, M. S.,Yun, C. S.,Afroze, S.,Radenahmad, N.,Bakar, M. S. A.,Saidur, R.,Taweekun, J.,Azad, A. K., (2020). Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. *Arab Journal of Basic and Applied Sciences***, 27** (1), 208-238.

105. Pallarés, J.,González-Cencerrado, A.,Arauzo, I., (2018). Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam. *Biomass and Bioenergy***, 115**, 64-73.

106. Yahya, M. A.,Al-Qodah, Z.,Ngah, C. Z., (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable and Sustainable Energy Reviews***, 46**, 218-235.

107. Iwanow, M.,Gärtner, T.,Sieber, V.,König, B., (2020). Activated carbon as catalyst support: precursors, preparation, modification and characterization. *Beilstein Journal of Organic Chemistry***, 16** (1), 1188-1202.

108. Rambabu, N.,Rao, B.,Surisetty, V.,Das, U.,Dalai, A., (2015). Production, characterization, and evaluation of activated carbons from de-oiled canola meal for environmental applications. *Industrial Crops and Products***, 65**, 572-581.

109. Balajii, M.,Niju, S., (2019). Biochar-derived heterogeneous catalysts for biodiesel production. *Environmental Chemistry Letters***, 17** (4), 1447-1469.

110. Dhankhar, R.,Hooda, A., (2011). Fungal biosorption–an alternative to meet the challenges of heavy metal pollution in aqueous solutions. *Environmental technology***, 32** (5), 467-491.

111. Iakovleva, E.,Sillanpää, M., (2013). The use of low-cost adsorbents for wastewater purification in mining industries. *Environmental Science and Pollution Research***, 20** (11), 7878-7899.

112. Sulyman, M.,Namiesnik, J.,Gierak, A., (2017). Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review. *Polish Journal of Environmental Studies***, 26** (3).

113. Crini, G.,Lichtfouse, E.,Wilson, L. D.,Morin-Crini, N., (2019). Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters***, 17** (1), 195-213.

114. Thommes, M.,Kaneko, K.,Neimark, A. V.,Olivier, J. P.,Rodriguez-Reinoso, F.,Rouquerol, J.,Sing, K. S., (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and applied chemistry***, 87** (9-10), 1051-1069.

115. Sahraie, N. R.,Kramm, U. I.,Steinberg, J.,Zhang, Y.,Thomas, A.,Reier, T.,Paraknowitsch, J.-P.,Strasser, P., (2015). Quantifying the density and utilization of active sites in non-precious metal oxygen electroreduction catalysts. *Nature communications***, 6** (1), 1-9.

116. Mashkoor, F.,Nasar, A., (2020). Magsorbents: Potential candidates in wastewater treatment technology–A review on the removal of methylene blue dye. *Journal of magnetism and magnetic materials***, 500**, 166408.

117. Chigondo, M.,Paumo, H. K.,Bhaumik, M.,Pillay, K.,Maity, A., (2019). Magnetic arginine-functionalized polypyrrole with improved and selective chromium (VI) ions removal from water. *Journal of Molecular Liquids***, 275**, 778-791.

118. Kera, N. H.,Bhaumik, M.,Pillay, K.,Ray, S. S.,Maity, A., (2018). m-Phenylenediamine-modified polypyrrole as an efficient adsorbent for removal of highly toxic hexavalent chromium in water. *Materials Today Communications***, 15**, 153-164.

119. Kera, N. H.,Bhaumik, M.,Ballav, N.,Pillay, K.,Ray, S. S.,Maity, A., (2016). Selective removal of Cr (VI) from aqueous solution by polypyrrole/2, 5-diaminobenzene sulfonic acid composite. *Journal of colloid and interface science***, 476**, 144-157.

120. Velempini, T.,Pillay, K.,Mbianda, X. Y.,Arotiba, O. A., (2019). Carboxymethyl cellulose thiol-imprinted polymers: Synthesis, characterization and selective Hg (II) adsorption. *Journal of Environmental Sciences***,** **79**, 280-296.

121. Ali, R. M.,Hamad, H. A.,Hussein, M. M.,Malash, G. F., (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering***,** **91**, 317-332.

122. Chen, J. P., *Decontamination of heavy metals: processes, mechanisms, and applications*. Crc Press: 2012.

123. Ugwu, E.,Tursunov, O.,Kodirov, D.,Shaker, L.,Al-Amiery, A.,Yangibaeva, I.,Shavkarov, F. In *Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review*, IOP Conference Series: Earth and Environmental Science, IOP Publishing: 2020; p 012166.

124. Kaprara, E.,Tziarou, N.,Kalaitzidou, K.,Simeonidis, K.,Balcells, L.,Pannunzio, E. V.,Zouboulis, A.,Mitrakas, M., (2017). The use of Sn (II) oxy-hydroxides for the effective removal of Cr (VI) from water: Optimization of synthesis parameters. *Science of the Total Environment***,** **605**, 190-198.

125. Simeonidis, K.,Kaprara, E.,Samaras, T.,Angelakeris, M.,Pliatsikas, N.,Vourlias, G.,Mitrakas, M.,Andritsos, N., (2015). Optimizing magnetic nanoparticles for drinking water technology: the case of Cr (VI). *Science of the Total Environment***,** **535**, 61-68.

126. Semerjian, L., (2010). Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated Pinus halepensis sawdust. *Journal of hazardous materials***,** **173** (1-3), 236-242.

127. Abbaszadeh, S.,Alwi, S. R. W.,Webb, C.,Ghasemi, N.,Muhamad, I. I., (2016). Treatment of lead-contaminated water using activated carbon adsorbent from locally available papaya peel biowaste. *Journal of Cleaner Production***,** **118**, 210-222.

128. Salam, O. E. A.,Reiad, N. A.,ElShafei, M. M., (2011). A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research***, 2** (4), 297-303.

129. Jasper, E. E.,Ajibola, V. O.,Onwuka, J. C., (2020). Nonlinear regression analysis of the sorption of crystal violet and methylene blue from aqueous solutions onto an agro-waste derived activated carbon. *Applied Water Science***, 10** (6), 1-11.

130. Rai, M.,Giri, B.,Nath, Y.,Bajaj, H.,Soni, S.,Singh, R.,Singh, R.,Rai, B., (2018). Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from almond shell: kinetics, equilibrium and thermodynamics study. *Journal of Water Supply: Research and Technology-Aqua***, 67** (8), 724-737.

131. Shimizu, S.,Matubayasi, N., (2021). Sorption: a statistical thermodynamic fluctuation theory. *Langmuir***, 37** (24), 7380-7391.

132. Huang, X.,Liu, Y.,Liu, S.,Tan, X.,Ding, Y.,Zeng, G.,Zhou, Y.,Zhang, M.,Wang, S.,Zheng, B., (2016). Effective removal of Cr (VI) using β-cyclodextrin–chitosan modified biochars with adsorption/reduction bifuctional roles. *RSC advances***, 6** (1), 94-104.

133. Al-Ghouti, M. A.,Da'ana, D. A., (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review. *Journal of hazardous materials***, 393**, 122383.

134. Saadi, R.,Saadi, Z.,Fazaeli, R.,Fard, N. E., (2015). Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. *Korean Journal of Chemical Engineering***, 32** (5), 787-799.

135. Moradi, O.,Fakhri, A.,Adami, S.,Adami, S., (2013). Isotherm, thermodynamic, kinetics, and adsorption mechanism studies of Ethidium bromide by single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube. *Journal of colloid and interface science***, 395**, 224-229.

136. Gao, Y.,Liu, K.,Kang, R.,Xia, J.,Yu, G.,Deng, S., (2018). A comparative study of rigid and flexible MOFs for the adsorption of pharmaceuticals: kinetics, isotherms and mechanisms. *Journal of hazardous materials***,** **359**, 248-257.

137. Kulal, P.,Krishnappa, P. B.,Badalamoole, V., (2021). Development of gum acacia based magnetic nanocomposite adsorbent for wastewater treatment. *Polymer Bulletin*, 1-28.

138. Kowanga, K. D.,Gatebe, E.,Mauti, G. O.,Mauti, E. M., (2016). Kinetic, sorption isotherms, pseudo-first-order model and pseudo-second-order model studies of Cu (II) and Pb (II) using defatted Moringa oleifera seed powder. *The journal of phytopharmacology***,** **5** (2), 71-78.

139. Hubbe, M. A.,Azizian, S.,Douven, S., (2019). Implications of apparent pseudo-second-order adsorption kinetics onto cellulosic materials: A review. *BioResources***,** **14** (3).

140. Hadgu, T.,Amare, M., (2016). Assessment of the level of chromium species in the discharged effluents of Haik and Debre Berhan tanneries in the Amhara Region using ICP-OES and UV-VIS spectrometry. *Ethiopian Journal of Science and Technology***,** **9** (2), 123-138.

141. Hamdy, A.,Mostafa, M. K.,Nasr, M., (2018). Zero-valent iron nanoparticles for methylene blue removal from aqueous solutions and textile wastewater treatment, with cost estimation. *Water Science and Technology***,** **78** (2), 367-378.

142. Zewdu, F.,Amare, M., (2018). Determination of the level of hexavalent, trivalent, and total chromium in the discharged effluent of Bahir Dar tannery using ICP-OES and UV–Visible spectrometry. *Cogent chemistry***,** **4** (1), 1534566.

143. Shah, A. J. Simultaneous Transformation of Hexavalent Chromium and Carbon Tetrachloride by Atomized Zerovalent Iron in Aqueous Medium. Howard University, 2019.

144. Ekpete, O.,Marcus, A.,Osi, V., (2017). Preparation and characterization of activated carbon obtained from plantain (Musa paradisiaca) fruit stem. *Journal of Chemistry***,** **2017**.

145. Bhavsar, (2018). Proximate analysis of selected non woody biomass. *International Journal of Current Microbiology and Applied Sciences***,** **7** (09), 2846-2849.

146. Al-Maliky, E. A.,Gzar, H. A.,Al-Azawy, M. G. In *Determination of Point of Zero Charge (PZC) of Concrete Particles Adsorbents*, IOP Conference Series: Materials Science and Engineering, IOP Publishing: 2021; p 012004.

147. Bakatula, E. N.,Richard, D.,Neculita, C. M.,Zagury, G. J., (2018). Determination of point of zero charge of natural organic materials. *Environmental Science and Pollution Research***, 25** (8), 7823-7833.

148. Ihsanullah,Al-Khaldi, F. A.,Abu-Sharkh, B.,Abulkibash, A. M.,Qureshi, M. I.,Laoui, T.,Atieh, M. A., (2016). Effect of acid modification on adsorption of hexavalent chromium (Cr (VI)) from aqueous solution by activated carbon and carbon nanotubes. *Desalination and Water Treatment***, 57** (16), 7232-7244.

149. Ituen, E.,Akaranta, O.,James, A., (2017). Evaluation of performance of corrosion inhibitors using adsorption isotherm models: an overview. *Chem. Sci. Int. J***, 18** (1), 1-34.

150. Repo, E., *EDTA-and DTPA-functionalized silica gel and chitosan adsorbents for the removal of heavy metals from aqueous solutions*. Lappeenranta University of TechnologyLaboratory of Green Chemistry: 2011.

151. Rasti, H.,Parivar, K.,Baharara, J.,Iranshahi, M.,Namvar, F., (2017). Chitin from the mollusc chiton: extraction, characterization and chitosan preparation. *Iranian journal of pharmaceutical research: IJPR***, 16** (1), 366.

152. Owalude, S. O.,Tella, A. C., (2016). Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. *Beni-suef university journal of basic and applied sciences***, 5** (4), 377-388.

153. Wu, B.,Peng, D.,Hou, S.,Tang, B.,Wang, C.,Xu, H., (2018). Dynamic study of Cr (VI) removal performance and mechanism from water using multilayer material coated nanoscale zerovalent iron. *Environmental Pollution***, 240**, 717-724.

154. Yunusa, U.,Kubo, A. I.,Abdullahi, Y.,Abdullahi, T.,Husaini, M., (2021). Hexavalent chromium removal from simulated wastewater using biomass-based activated carbon: kinetics, mechanism, thermodynamics and regeneration studies. *Algerian Journal of Engineering and Technology***, 4**, 30-44.

155. Riyanti, F.,Hariani, P. L.,Purwaningrum, W.,Elfita, E.,Damarril, S. S.,Amelia, I., (2018). The synthesis of MnFe2O4-activated carbon composite for removal of methyl red from aqueous solution. *Molekul***, 13** (2), 123-132.

156. Kumar, S.,Shahnaz, T.,Selvaraju, N.,Rajaraman, P. V., (2020). Kinetic and thermodynamic studies on biosorption of Cr (VI) on raw and chemically modified Datura stramonium fruit. *Environmental monitoring and assessment***, 192** (4), 1-24.

157. Benderdouche, N.,Bestani, B.,Hamzaoui, M., (2018). The use of linear and nonlinear methods for adsorption isotherm optimization of basic green 4-dye onto sawdust-based activated carbon. *Journal of Material Environmental Science***, 9** (4), 1110-1118.

158. Pehlivan, E.,Kahraman, H., (2011). Sorption equilibrium of Cr (VI) ions on oak wood charcoal (Carbo Ligni) and charcoal ash as low-cost adsorbents. *Fuel Processing Technology***, 92** (1), 65-70.

159. Jain, M.,Garg, V.,Kadirvelu, K., (2009). Chromium (VI) removal from aqueous system using Helianthus annuus (sunflower) stem waste. *Journal of hazardous materials***, 162** (1), 365-372.

160. Gode, F.,Atalay, E. D.,Pehlivan, E., (2008). Removal of Cr (VI) from aqueous solutions using modified red pine sawdust. *Journal of Hazardous Materials***, 152** (3), 1201-1207.

161. Premkumar, M.,Abinandan, S.,Sowmya, V.,Shanthakumar, S., (2015). Efficacy of Eleusine coracana (L.) Gaertn (Ragi) husk for adsorption of chromium (VI): A study using response surface methodology. *Environmental Progress & Sustainable Energy***, 34** (1), 139-145.

162. Mekuria, D.,Diro, A.,Melak, F.,Asere, T. G., (2022). Adsorptive Removal of Methylene Blue Dye Using Biowaste Materials: Barley Bran and Enset Midrib Leaf. *Journal of Chemistry***, 2022**.

163. Muhammad, A. S., (2020). Adsorption of methylene blue onto modified agricultural waste. *Moroccan Journal of Chemistry***, 8** (2), 8-2 (2020) 412-427.

164. Liu, L.,Fan, S.,Li, Y., (2018). Removal behavior of methylene blue from aqueous solution by tea waste: kinetics, isotherms and mechanism. *International journal of environmental research and public health***, 15** (7), 1321.

165. Shakya, A.,Agarwal, T., (2019). Removal of Cr (VI) from water using pineapple peel derived biochars: Adsorption potential and re-usability assessment. *Journal of molecular liquids***, 293**, 111497.

166. Tu, B.,Wen, R.,Wang, K.,Cheng, Y.,Deng, Y.,Cao, W.,Zhang, K.,Tao, H., (2020). Efficient removal of aqueous hexavalent chromium by activated carbon derived from Bermuda grass. *Journal of colloid and interface science***, 560**, 649-658.

7 APPENDIX

APPENDIX 7A: Solution Preparation

1. The preparation of 1000mg/L Potassium dichromate Stock solution from the analytical grade of potassium dichromate ($K_2Cr_2O_7$).That is Potassium dichromate($K_2Cr_2O_7$) has a molecular weight=2×39+2×52+7×16=294 g/mole, which means 104g of Cr(VI) is available in 294 g of $K_2Cr_2O_7$. Therefore,1g of Cr(VI) is available in (294/104)×1=2.827 g of $K_2Cr_2O_7$ was taken and diluted with distilled water in 1000mL of volumetric flask.

2. MB stock solution was prepared from 0.5% MB solution that is the concertation becomes 5000ppm stock. From this the experimental solutions were prepared with serial dilution.

3. The preparation of Cr(VI) & MB standard & working solution from a stock solution of 1000ppm(M_1) ,Cr(VI) & MB was as follows.

   From the stock solution prepare 100ppm Cr(VI)& MB by taking 10ml stock solution in 100ml volumetric flask. The required diluted concentration of Cr(VI) & MB, that is (M_2) = (2ppm,4ppm,6ppm,8ppm and 10ppm for working solution & 1ppm,5ppm,10ppm,15ppm &20ppm for standard solution) were prepared by usig dilution law , $M_1V_1=M_2V_2$ for example for 2ppm the volume is equal to 2ppm×50ml/100ppm=1ml.

4. Preparation of 0.1M KOH was by the dissolution of 0.28 g with distilled water in a 50ml flask

5. Preparation of 0.1M HCl, 0.5 ml of Conc, hydrochloric acid was taken in a cleaned and dried 50ml volumetric flask and then makes up the volume up to 50ml with distilled water

6. Preparation of 1,5-Diphenyl carbazide (DPC) Complexing agent,0.25g of 1,5-Diphenyl carbazide (DPC) was diluted in 50ml of acetone then add a distilled water in 100 volumetric flask

APPENDIX 7B: Characterization of ACDWHL

- **Proximate Analysis of ACDWHL**
  - ✓ WB=weight of the sample before drying/heating
  - ✓ WA= weight of the sample after drying/heating
  - ✓ $\bar{X}$=Mean
  - ✓ SD=Standard deviation
  - ✓ Weight of the three crucibles (29.56 g, 28 g & 29 g)
- Moisture & Ash Content Calculation

Mc (%) = $\frac{(WB-WA)\times 100}{WB}$ **Ac (%)** = $\frac{(WB-WA)\times 100}{WB}$

Table7. 1 Moisture & Ash Content.

Trial	**WB(g)**	**WA(g)**	**Mc (%)**	**WB(g)**	**WA(g)**	**Ac (%)**
1	2	1.85	7.5	2	1.8	10
2	2	1.9	5	2	1.78	11
3	2	1.87	6.5	2	1.75	12.5
			$\bar{X}$=6.3			$\bar{x}$=11.2
			SD=1.26			SD=1.259

- Volatile Mater Content (Vc%) & Carbon Yield (Y%):

Vc = $\frac{(WB-WA)\times 100}{WB}$ **Y%** = $\frac{WA\times 100}{WB}$

Table7. 2 Volatile Mater Content (Vc%) & Carbon Yield (Y%).

Trial	**WB(g)**	**WA(g)**	**Vc (%)**	**WB(g)**	**WA(g)**	**Y%**
1	2	1.5	25	8	4.63	57.88
2	2	1.45	27.5	8	4.5	56.3
3	2	1.41	29.5	8	4.4	55
			$\bar{X}$=27.3			$\bar{X}$=56.4
			SD=3.2			SD=1.4

- The Point of Zero Charge:

Table7. 3 Point of Zero charge of ACDWHL data.

Initial pH	**Final pH**	**ΔPH**
1	1.8	0.8
2	2.6	0.6
3	4	1
4	4.6	0.6
5	5.5	0.5
6	5	-1
7	5.8	-1.2
8	6.44	-1.56
9	7.4	-1.6
10	8.1	-1.9
11	9	-2
12	9.5	-2.5

APPENDIX 7C: Effect of Adsorption parameters

Table7. 4 Cr (VI) & Methylene blue standard concentration with absorbance.

Initial concentration (ppm)	**Absorbance**	
	chromium (VI)	Methylene blue
1	0.545	0.12
5	1.028	0.5
10	1.322	0.92
15	1.657	1.36
20	2.035	1.78

Table7. 5 Effect of pH on chromium (VI) & MB removal by ACDWHL.

PH		**Absorbance**		**Ce (ppm)**		**% Removal**		**qe (mg/g)**	
Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
1	6	1.135	0.34	2.5	3.352	75	66.48	1.88	1.7
2	8	1.124	0.234	2.46	2.133	75.4	78.67	1.89	1.97
3	10	1.174	0.13	2.6	0.938	73.97	90.62	1.85	2.27
4	12	1.195	0.144	2.66	1.0988	73.4	89.012	1.84	2.23
5	14	1.213	0.153	2.71	1.202	72.9	87.97	1.83	2.2
6		1.265		2.85		71.45		1.79	
7		1.297		2.94		70.57		1.77	
8		1.321		3.01		69.9		1.75	

Table7. 6 Effect of concentration on chromium (VI) & MB removal by ACDWHL.

Concentration (ppm)	**Absorbance**		**Ce (ppm)**		**% Removal**		**qe (mg/g)**	
	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
2	0.347	0.09	0.311	0.478	84.4	95.2	0.4	0.4
4	0.467	0.108	0.64	0.685	83.9	93.15	0.8	0.8
6	0.675	0.114	1.22	0.754	79.67	92.46	1.2	1.3
8	0.912	0.12	1.877	0.823	76.5	91.77	1.5	1.8
10	1.17	0.13	2.6	0.938	74.08	90.62	1.85	2.3

Table7. 7 Effect of dose on chromium (VI) & MB removal by ACDWHL.

Dosage (mg)	**Absorbance**		**Ce (ppm)**		**% Removal**		**qe (mg/g)**	
	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
50	1.17	0.212	2.6	1.88	74.08	81.2	7.4	8.12
100	1.0547	0.196	2.21	1.696	77.9	83.04	3.9	4.15
150	1.026	0.146	2.19	1.122	78.1	88.78	2.6	2.96
200	1.032	0.125	2.209	0.88	77.91	91.2	1.95	2.28
250	1.031	0.125	2.206	0.88	77.94	91.2	1.6	1.82

Table7. 8 Effect of time on chromium (VI) & MB removal by ACDWHL.

Time min	**Absorbance**		**Ce (ppm)**		**% Removal**		**qe (mg/g)**	
	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
30	1.315	0.211	2.99	1.87	70.06	81.3	1.75	2.0325
60	1.235	0.172	2.77	1.42	72.28	85.8	1.81	2.145
90	1.185	0.126	2.63	0.893	73.67	91.07	1.84	2.277
120	1.138	0.128	2.5	0.915	74.97	90.85	1.88	2.27
150	1.154	0.129	2.55	0.926	74.5	90.74	1.863	2.267
180	1.16	0.127	2.56	0.903	74.36	90.97	1.86	2.274

Table7. 9 Adsorption isotherm of chromium (VI) & MB using ACDWHL.

Concentration	**$\bar{x}$ of Ce(ppm)at (120,150,180) & (90,120,150)min**		**qe(mg/g)**		**1/ce**		**1/qe**		**Logce**		**Logqe**	
	Cr^{+6}	MB	Cr^{+6}	MB	Cr^{+6}	MB	Cr^{+6}	MB	Cr^{+6}	MB	Cr^{+6}	MB
2	0.3	0.5	0.57	0.38	3.3	2	1.75	2.63	-0.5	-0.3	-0.24	-0.42
4	0.6	0.7	1.13	0.83	1.7	1.43	0.89	1.2	-0.22	-0.15	0.05	0.08
6	1.02	0.75	1.7	1.32	0.98	1.33	0.59	0.76	0.009	-0.13	0.23	0.12
8	1.8	0.8	2.07	1.8	0.55	1.25	0.48	0.56	0.26	-0.09	0.32	0.26
10	2.5	0.9	2.5	2.28	0.4	1.1	0.4	0.44	0.4	-0.05	0.4	0.36

Table7. 10 The kinetic studies of Adsorption of chromium (VI) & MB using ACDWHL.

Time min	qt(mg/g)		qe(mg/g)		t/qt		Log (qe-qt)	
	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB	Cr (VI)	MB
30	1.7	2.0325	1.85	2.3	17.65	14.76	-0.8	-0.57
60	1.74	2.145	1.85	2.3	34.5	27.97	-0.96	-0.81
90	1.8	2.277	1.85	2.3	50	39.5	-1.3	-1.64
120	1.84	2.27	1.85	2.3	65.2	52.86	-2	-1.53
150	1.823	2.267	1.85	2.3	82.3	66.17	-1.57	-1.48
180	1.82	2.274	1.85	2.3	98.9	79.16	-1.5	-1.59

Table7. 11 Real sample experimental data.

TS	**Absorbance**				**concentration (ppm)**				**%Removal**		**qe(mg/g)**	
TW W	BT WW	AT WW	BTA WW	ATA WW	BT WW	AT WW	BTA WW	ATA WW	BTA WW	ATA WW	BTA WW	ATA WW
	1.69	0.75	1.29	0.51								
	1.87	0.95	1.3	0.74								
	1.98	1.25	1.55	0.9								
$\bar{x}$	1.85	0.99	1.38	0.7	4.47	3.16	2.08	1.3	53.4	58.8	0.8	0.62
SD	0.15	0.25	0.15	0.2								
TX WW	0.81	0.24	0.71	0.14								
	1.12	0.14	0.61	0.08								
	0.9	0.16	0.46	0.09								
$\bar{x}$	0.95	0.18	0.59	0.09	10.3	1.52	6.2	0.5	40.4	67.3	1.03	0.26
SD	0.16	0.05	0.13	0.02								