ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

DEPARTMENT OF CHEMISTRY

REMOVAL OF HEXAVALENT CHROMIUM BY ADSORPTION USING STEM EXTRACT MATERIAL FROM WATER HYACINTH

BY

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Removal of Hexavalent Chromium by Adsorption Using Stem Extract Material from Water Hyacinth

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A thesis submitted to the Department of Chemistry, Addis Ababa University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry.

July 2021

Addis Ababa

Declaration

I hereby declare that this research study is my own original work and that all references have been correctly indicated and acknowledged, and it has been submitted to Analytical Chemistry, Addis Ababa University. The thesis "Removal of Hexavalent Chromium by Adsorption Using Stem Extract Material from Water Hyacinth" is conducted under the supervision of Dr. Solomon Mehretie, Department of Chemistry, Addis Ababa University, Ethiopia.

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This thesis has been submitted for examination with my approval as university advisor.

Advisor's Name _____

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Place and date of submission: Natural and computational sciences

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APPROVAL OF THE THESIS

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Abstract

Environmental pollution is one of the public issues for both developed and developing countries due to population growth, industrialization, urbanization and economic development. Toxic heavy metals are the most common inorganic pollutants to the environment. Chromium is one of the toxic heavy metal identified by world health organization (WHO) as major public health concern. This study focus on the removal of hexavalent chromium (Cr(VI)) on a stem extract material from water hyacinth. The physicochemical properties like crude fat, crude protein, crude fiber, moisture and ash contents of the adsorbent material were investigated. The effects of various variables such as initial concentration of Cr(VI), contact time, adsorbent dosage and pH, which influence the adsorption process were studied using UV-visible spectrophotometer. The optimum conditions were found to be 5.0 mg for adsorbent dose, and 240 and 210 min for contact times in the unmodified (SEMWH) and modified (SEMWH-AN) adsorbent materials, respectively. The adsorption capacities were found to be of 31.82 for SEMWH and 35.64 mg/g for SEMWH-AN adsorbents. In addition, maximum removal percentages of Cr(VI) were 96.0% and 99.9% for the aforementioned adsorbents, respectively. The experimental results show that the adsorption of Cr(VI) on adsorbents follow Langmuir isotherm model and obey pseudo-second-order kinetics.

KEYWORDS: Stem extract material from water hyacinth, adsorbent, polyaniline, hexavalent chromium and UV-visible spectroscopy.

Contents

List of Figures

List of Tables

Abbreviations

AN	Aniline
DNA	Deoxyribonucleic acid
DWHR	Dried water hyacinth roots
EPA	Environmental Protection Agency
FT-IR	Fourier-transform infrared spectroscopy
GBPs	Grafted banana peel
LP	Litchi peel
MLP	Modified litchi peel
MS	Mean squares
N	Number of trials
PANI	Polyaniline
PFO	Pseudo first order
PSO	Pseudo second order
q_e	Adsorption capacity
%R	Removal percentage
RPD	Relative percent difference
RSD	Relative standard deviation
SE Mean	Standard error of mean

SEM	Stem of water hyacinth
SEMWH	Stem extracted materials from water hyacinth
SEMWH-AN	Stem extracted material from water hyacinth copolymer with aniline
SD	Standard deviation
SS	Sum of squares
WHO	World Health Organization
WWS1	Wastewater sample
WWS2	Wastewater sample 2

1. Introduction

Environmental pollution is one of the major concern in the world due to urbanization, industrialization, high population density, improved living conditions and economic development **[1]**. Large amount of environmental pollutants mostly toxic heavy metals are directly or indirectly discharges to the environment through natural or anthropogenic activity, and which are very harmful to the human body and another life forms even in low concentrations as there is no effective removal mechanism **[1, 2]**. Natural sources of heavy metals in the environment include natural weathering of rocks, soil erosion and volcanic eruptions, and anthropogenic activities are metallurgical processes, industry, agriculture, printing, photographic materials, combustion of fossil fuel, forest fires, mining activity, automobile emissions and sewage **[2, 3]**.

From the eco-toxicological point of view, chromium (Cr) is one of the most toxic heavy metals to living organisms with different adverse health effects in humans, animals, plants and microorganisms **[4]**. Chromium (Cr) is widely exists in industrial wastewater from electroplating, petroleum refining, alloy manufacturing and battery production, that contaminates the soil and water resource **[5]**. Chromium exists mainly as Cr(III) and Cr(VI) in the natural environment, among which Cr(VI) is much more poisonous or very lethal, soluble and mobile than Cr(III) **[6]**. Hexavalent chromium could cause poisonous and harmful effects on humans and animals **[7]**. The most form of Cr(VI) ions ingestion into plant and animal metabolism is through water and food consumptions.

According to EPA, the permissible limit of hexavalent chromium in the drinking water is 0.1 mg/L **[8]**. WHO permissible limit of total chromium in wastewater is 0.1 mg/L and hexavalent

chromium is 0.05 mg/L, respectively **[9]**. Several reports have revealed that the accumulation of chromium metal in human above the WHO permissible limit **[10]**. Hexavalent chromium affects various components of the immune system, and can cause several health effects such as lung cancer, kidney failure, DNA damage, reproductive and respiratory problems **[11-15]**.

Therefore, toxic heavy metals must be reduced or removed from the environment by using different technologies or methods. Some of these methods are chemical precipitation **[16]**, ion-exchange **[17]**, reverse osmosis **[18]**, coagulation, membrane separation and adsorption **[19]**. Among these conventional techniques, adsorption is one of the most promising and frequently used methods due to their selectivity, low cost, ease of use, high efficiency (even when these metals are in low concentration) and the possibility of reusing the materials involved **[20]**.

1.1. 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. Wastewater contains liquid as well as solid waste. Some of these wastewater or contaminated water with heavy metals effluent are untreated or inadequately treated before being discharged to the environments, which become a worrisome phenomenon due to its impact on environmental health and safety. Now a days, urban agriculture is developing at rapid rate to contribute food and nutrition security in most part of the world.

The farmers in urban areas of developing countries including Ethiopia, depends on wastewater sources to irrigate high-value edible crops for urban markets. Vegetables or high- valued edible

crops accumulate heavy metals depending upon plant species and the efficiency of different parts of the plants by either plant uptake or soil-to-plant transfer factors of the metals and type of plant species with their stage of maturity **[21]**. In this way the toxic heavy metals enter the food chain of animals and humans. Some heavy metals are important as trace elements to maintain human body metabolism but at higher concentrations which courses varies adverse health effects and even death. There are no local studies for the removal of toxic heavy metals from wastewater using stem extract material from water hyacinth. Therefore, this study focuses on the removal of hexavalent chromium from tannery wastewater by adsorption, using stem extract material from water hyacinth as an adsorbent.

1.2. Objectives

1.2.1. General objective

The main objective of this research is to study the removal of hexavalent chromium from tannery wastewater by adsorption using stem extract material from water hyacinth.

1.2.2. Specific objectives

The specific objectives of this study includes;

1. To study the effect of pH, adsorbent dosage mass, initial concentration and contact time for removal mechanism.
2. To study removal of hexavalent chromium from tannery wastewater by adsorption process.
3. To study the efficiency of adsorbent material for wastewater treatment.
4. To study some physicochemical properties of the stem extract material from water hyacinth.

1.3. Scope of the study

This study was focused on the removal of hexavalent chromium from tannery wastewater using stem extract material from water hyacinth. The effect of adsorbent dosage mass, contact time, initial concentration and pH on the removal efficiency and adsorption capacity of Cr(VI) were conducted using UV-Vis spectrophotometer. The adsorption experiments were investigated in triplicate and average tests were reported.

2. Literature Review

2.1. Heavy metals

Heavy metals have relatively high density and are toxic even at low (ppb) levels of concentrations **[22]**. Some of toxic heavy metals are As, Hg, Cr, Pb, Cd and so on. These toxic heavy metals are released into the agricultural field by both natural and anthropogenic sources. Vegetables or agricultural crops which grow on the contaminated area or environment can absorb theses toxic heavy metals through air, soil, and water. Heavy metal polluted soil, water and plants causes different impacts to environmental and public health **[11,12]**. Unlike organic pollutants, heavy metals are non-biodegradable and have tendency to accumulate in living beings, and most of them are known to be potential carcinogens. Long-term exposure of the body to heavy metal can lead to various adverse health hazards like muscular, physical and neurological degenerative processes. From those metals, chromium is one of the most toxic and carcinogenic heavy metal.

2.2. Chromium

Chromium is transition metallic element with the symbol Cr, atomic number of 24 and the electron configuration for chromium Cr is [Ar] $3d^5 4s^1$. It is the first element in group six, period four and block d in the periodic table. Chromium is a naturally occurring element found in rocks, plants, soil, animals and in volcanic dust and gases. Chromium is a lustrous, brittle, hard metal, silver-gray in colour and it can be highly polished. The most common oxidation state of chromium are; Cr(VI) and Cr(III) these are strongly acidic oxides. No taste or odor is associated with chromium compounds. Cr(III) occurs naturally in the environment and is an essential nutrient at low concentration but Cr(VI) and Cr(0) are generally produced by industrial processes. Cr(0), Cr(III)

and Cr(VI) which occurs in metallic or native chromium, chromic, and chromate and dichromate compounds, respectively.

2.2.1. Uses of chromium

Chromium is used on large scale in the metallurgical and chemical industries. The metallurgical industries use chromium for the production of stainless steel, alloy cast iron and nonferrous alloys plating steel for example on cars and bicycles, aircraft, produces a smooth, silver finish that is highly resistant to corrosion. Chromium is used in the chemical industries for pigments for their vivid green, yellow, red and orange colors and dyes, as a catalyst, petrochemical, and nuclear sectors. Chromium metal in the form of Cr(0), is used for making steel. Chromium in the form of Cr(VI) and Cr(III) are also used for chrome plating, dyes and pigments, textile manufacturing, leather tanning and wood preserving. Cr(III) is essential element to human to have normal glucose, protein and fat metabolism.

2.2.2. Sources of chromium

Hexavalent and trivalent chromium are released to the environment primarily from different point sources which are natural and anthropogenic activities **[2, 3]**. The anthropogenic sources of chromium has increased rapidly due to industrial revolution because Cr(VI) compounds are well known laboratory reagents in various industrial processes and also used as intermediates for synthesis of other compounds. Industries use much amount of water during the process of raw materials into products and generate a large volume of wastewater, which contains high concentrations of various types of pollutants. Industrial, domestic as well as commercial sources include; airborne emissions, cement dust, contaminated landfill, effluents from chemical plants,

asbestos lining erosion, road dust from catalytic converter erosion and asbestos brakes, tobacco smoke **[23]**. Tanning industry is one of the source of chromium in the world. The tannery industry uses chromium for converting raw materials or hides and skins into leather for producing articles like bag, shoe, belt, suitcase, jacket and wallet.

2.2.3. Chromium compounds

Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Some stable compounds of chromium are Cr(V), Cr(IV), Cr(I) and Cr(0). In the Cr(VI), the most important species formed by chromium are the chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions. These ions are very important for the basis of industrial salts. Sodium chromate (Na_2CrO_4) and sodium dichromate ($Na_2Cr_2O_7$) are the most common compounds used in metal surface treatment, in leather tanning, and as catalysts in various industrial processes. Chromic acid (H_2CrO_4) used for analytical reagent, leather and tannery industry. Potassium dichromate ($K_2Cr_2O_7$) is also used for glass cleaning, oxidizing agent and chrome plating as shown in the **Figure 1.**

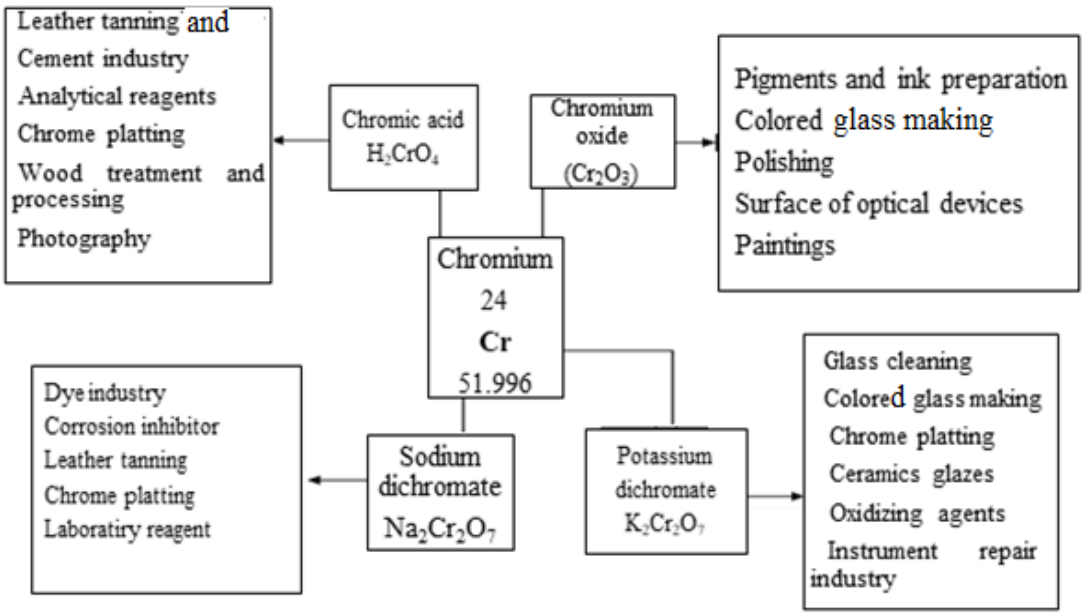

Figure 1. Most common form of chromium compounds and their uses.

2.2.4. Environmental and health impacts of chromium

Environmental pollution is one of the main concern to human being because every person is frequently exposed this pollution every day, through drinking water, breathing air, eating food. Chromium is one of the most common toxic element present in the environment because it released directly or indirectly to the agricultural field or the environment from different sources. The amount of chromium in the soil rises, this can still lead to higher concentrations in vegetable crops. Chromium metal is an essential element to human body in low concentration, but Cr(VI) is genotoxic carcinogenic to microorganism, plants, animals and humans, due to its oxidation state and solubility **[24]**. Cr(VI) compounds, which have high mobility in water, strong oxidizing agents, and thus leads to be irritating and corrosive, appear to be much more toxic systemically than Cr(III) compounds, given similar amounts and solubilities.

Trivalent chromium is less toxic, more stable and insoluble, while hexavalent chromium is extremely toxic even at low concentration and highly soluble. Hexavalent chromium can alter genetic materials and cause cancer, blood pressure, kidney failure, mental retardation, pneumonia, asthma, ulcerations of the skin, bronchitis, hepatic and renal damage, tissue necrosis, weakened immune system, damage the respiratory tract in short term (acute) and long term (chronic) inhalation exposures through people breathing it, ingesting it in food or water, or direct contact with the skin.

Table 1. Some of health effects of chromium toxicity.

Toxicity	Health Effects	References
Carcinogenicity	Lung and nasal cancer are associated with the exposure through inhalation and ingestion of drinking water.	**[11]**
Toxicity and mutagenicity	Damage the DNA, gene mutation, sister chromatid exchange, cell impairment, chromosomal aberration	**[12,13]**
Reproductive and developmental	Birth defects and decreased spermatogenesis and histopathological alterations	**[14]**
Respiratory	Ulceration and perforation of nasal septum and irritation of upper airways	**[15]**

2.2.5. Removal of chromium by adsorption

According to the Environmental Protection Agency (EPA), hexavalent chromium is considered priority pollutant and must be eliminated or reduced using various treatment technologies from any water body that may or may not come in to contact with the environment **[25]**. Adsorption technique is the one which is selected to remove hexavalent chromium from tannery wastewater. Adsorption is a surface property and an attachment of a particular compound at the surface of a solid object by physical forces or by chemical bonds **[26]**.

Adsorption is also defined as a process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorbate is a substance which is adsorbed on the surface of adsorbent material followed by adsorption reaction onto the sites. An adsorbent is a substance that is usually porous in nature with high surface area or form of moldings, spherical pellets that can adsorb substances onto its surface with the help of intermolecular forces **[27]**. Depending on the substance being deposited and adsorbed, adsorption is classified into two types physisorption and chemisorption. Physisorption is also known as physical adsorption and it is an exothermic process and gas is accumulated on the solid surface due to weak force, known as Van der Waals forces **[28]**. Chemisorption is also known as chemical adsorption and adsorption takes place in adsorbed substance that is held by chemical bonds. Chemisorption has high specificity and it takes place only if there is a chemical bonding between the adsorbent and the adsorbate. The difference between chemisorption and physisorption processes are listed in **Table 2**.

Table 2. Comparison of physical and chemical adsorption.

	Physical adsorption	Chemical adsorption
Adsorption force	Van der Waals force	Chemical bond force
Adsorption layer	Single or multiple layers	Single layer
Adsorption rate	Fast	Slow
Adsorption heat	Low	High
Selectivity	Nonselective adsorption	Selective adsorption

The removal of Cr(VI) from the synthetic aqueous solution using chemically modified dried water hyacinth roots was evaluated **[29]**. The removal percentage and the adsorption capacity influencing parameters such as effect of contact time, adsorbent dosage, initial concentration and the effect of pH were examined. The optimum condition for the removal of Cr(VI) was found at pH 3.0, contact time 100 min, adsorbent dosage 5 mg/L, and the adsorption capacity 1.28 mg/g.

Grapefruit peelings as a promising biosorbent for the removal of leather dyes and hexavalent chromium were evaluated **[30]**. The optimum condition for the adsorption of Cr(VI) ion was at pH 5.5, adsorbent dose 1 g/L, contact time 400 min adsorption capacity 39.06 mg/g , and removal percentage 99.95%. The removal of hexavalent chromium from aqueous solution was examined using low-cost agroindustrial adsorbents such as lime peel and pineapple core wastes **[31]**. The maximum adsorption capacities for these sorbents were 9.20 and 8.8 mg/g, respectively, at 24 h equilibrium time. The resulting optimal conditions were: initial solution pH 2.01, biosorbent dosage 30 g/L and temperature 30 ^{o}C.

The removal of hexavalent chromium from aqueous medium was evaluated using low-cost adsorbent derived from the coconut shell **[32]**. The coconut shell as biosorbent was modified by physical activation using carbon dioxide (CO_2), ozone (O_3) and steam (H_2O). The adsorption conditions for the removal percentage and adsorption capacity of Cr(VI) were found at pH 2.0, contact time 140 min, adsorbent dosage 1 mg/L, adsorption capacity 9.43 mg/g and removal percentage 94%. The removal of Cr(VI) from aqueous solutions by modified litchi peel (MLP) was investigated **[33]**. The optimal pH condition and optimum dosage, equilibrium time, for the adsorption of Cr(VI) were found to be 1.0 and 8.0 g/L, 100 min, respectively. The adsorption isotherm models namely Langmuir and Freudlich models were used to study the adsorption process. The result provided better correlation to Langmuir model for the adsorption of Cr(VI) on litchi peel (LP) and modified litchi peel (MLP). The maximum adsorption at equilibrium for MLP is 9.55 mg/g, while for LP it is only 7.05 mg/g. The adsorption kinetics of the study followed pseudo-second-order model.

The adsorptive removal of hexavalent chromium from aqueous solutions was investigated by acrylonitrile grafted banana peels (GBPs) **[34]**. The optimum conditions for adsorption of Cr(VI) were found to be at pH 3.0, adsorbent dose 4.0 g/L, concentration 400 mg/L and contact time of 120 min. The removal percentage of Cr(VI) onto grafted banana peels (GBPs) was recorded to be 96% and the adsorption kinetics was fitted to pseudo-second order kinetic model.

2.3. Water hyacinth as adsorbent material

Water hyacinth *(Eichhornia crassipes)* is the most rapidly growing, very productive free-floating aquatic plant, and widely distributed species that originated in the Amazon, South America **[35].** The entry of water hyacinth into Africa, Asia, Australia, and North America was facilitated by

human activities **[36]**. Specifically, Africa has been affected by the introduction and widespread of water hyacinth, facilitated in part due to a lack of controlling and removing mechanisms. Water hyacinth reproduces itself very quickly by short runner stems (stolons) that radiate from the base of the plant to form daughter plants, and also reproduces by seed and it has the ability to covers large water bodies in different countries within a short period of time.

Lake Tana, Amhara region in Ethiopia is the one which is covered by water hyacinth as shown in **Figure 2**. Water hyacinth has a potential to degrade water quality, water volume, aquatic organisms and biological diversity by blocking photosynthesis, which greatly reduces oxygen levels in the water **[37]**. Water hyacinth affects biodiversity, ecosystem, human and animal health, and socio-economic development significantly **[38]**. Till now a lot of money and resources are spent in order to destroy the water hyacinth to prevent the water body from drying. Nowadays, it has different applications, including organic fertilizer, mulching, biofuel, and to clean the sewage. There are so many results found in the scientific literature, for the removal of hexavalent chromium by adsorption technique but there is the limited study to remove hexavalent chromium by adsorption using stem extract material from water hyacinth as adsorbent. Water hyacinth has the ability to take up or accumulate several toxic metals in the root, stem and leaf parts under controlled conditions and also has the ability to convert the toxicity of heavy metals from chemically-active toxic to inactive and nontoxic forms **[39].**

Figure 2. Photographic representation of water hyacinth in Lake Tana.

2.3.1. Uses of stem extract material from water hyacinth

Stem of water hyacinth consisting of high percentage of water, fibrous tissue, high energy and protein content can be used for a variety of useful applications. A number of possible uses includes phytoremediation or wastewater treatment, bio-fuel production, biomass and energy, compost and fertilizer, biopolymer and animal feed **[40]**. Water hyacinth biomass has been used as the adsorbents to remove heavy metals and the metal nanoparticles for pharmaceutical industries, photo catalysts, and biosensors due to its high cellulose, and has high proteins **[41]**. Different literatures indicate that water hyacinth has the ability to clean up various contaminated water specially water contaminated with toxic heavy metals **[42]**.

3. Materials and Methods

3.1. Study area

The adsorbent material was collected from Lake Tana and the wastewater was also collected from Bahir Dar tannery industry in Amhara region, Ethiopia. This study was conducted in Addis Ababa University, Ethiopia. In the Department of Chemistry, analytical chemistry laboratory from October 2020 to July 2021.

3.2. Apparatus and instruments

Electrical balance (ae ADAM) , chopper (mechanical grinder), mortar and pestle, shaker (KS Oscillator, China), centrifugation, beakers, conical flask, measuring cylinder, filter paper, water bath, 2510 Branson ultrasonic, oven, muffle furnace, suction filtration, nitrogen generator (PEAK scientific), pH meter (Jenway, UK), Agilent Cary 60 UV-Vis spectrophotometer, fourier-transform infrared spectroscopy (spectrum 65 FT-IR) (PerkinElmer), Kjeldahl, fibertec ^{TM} 8000 auto fiber analysis system (FOSS, China), soxtec ^{TM} 8000 extraction system (FOSS, China), aluminum cap, desiccator, cotton (defatted) and thimbles were used.

3.3. Chemicals and reagents

Potassium dichromate ($K_2Cr_2O_7$) (Carelabmed, India), sulfuric acid (H_2SO_4) (95-97%, (Fluka, Germany), hydro chloric acid (HCl) 37% (Fluka, Germany), nitric acid (HNO_3) 69% (Fluka), sodium hydro oxide (NaOH) assay > 97% (RPE, ACS-ISO for analysis), ammonium persulfate ($(NH_4)_2S_2O_8$) assay =99% (BDH, England), aniline 99.5% (Aldrich A.C.S. reagent), ethanol, 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$ assay > 99% (Sigma Aldrich, India), acetone > 99% (Fisher

chemical) and hydrogen peroxide (30%), n-Hexane, antifoaming agent, n-octanol, 1% boric acid and catalyst (K_2SO_4 and $CuSO_4$ X $5H_2O$) (VELP Scientifica), sodium azide (NaN_3), methyl red indicator and ammonium hydroxide (NH_4OH) (BDH, China) were used.

3.4. Sample collection and preparation

The stem part of water hyacinth or an adsorbent material was collected from Lake Tana in Amhara region, Ethiopia. The real samples were also collected from Bahir Dar tannery wastewater and leveled as WWS1 and WWS2.

3.4.1. Preparation of adsorbent

The stem of water hyacinth was washed with tape water and socked 2:1 ratio of distilled water to weight of stem of water hyacinth for 30 min. The socked sample was ground using chopper (mechanical grinder) and the pH was adjusted at pH 9, then the separated clean solution from residue was again adjusted at pH 2 using 1 M NaOH and 1 M HCl, respectively. The solution was heated on water bath at 80 ^oC for 5 min, filtered with suction filtration and the product was dried using oven at 60 ^oC overnight then it was ground using mortar and pestle for further analysis as shown in the **Figure 3.**

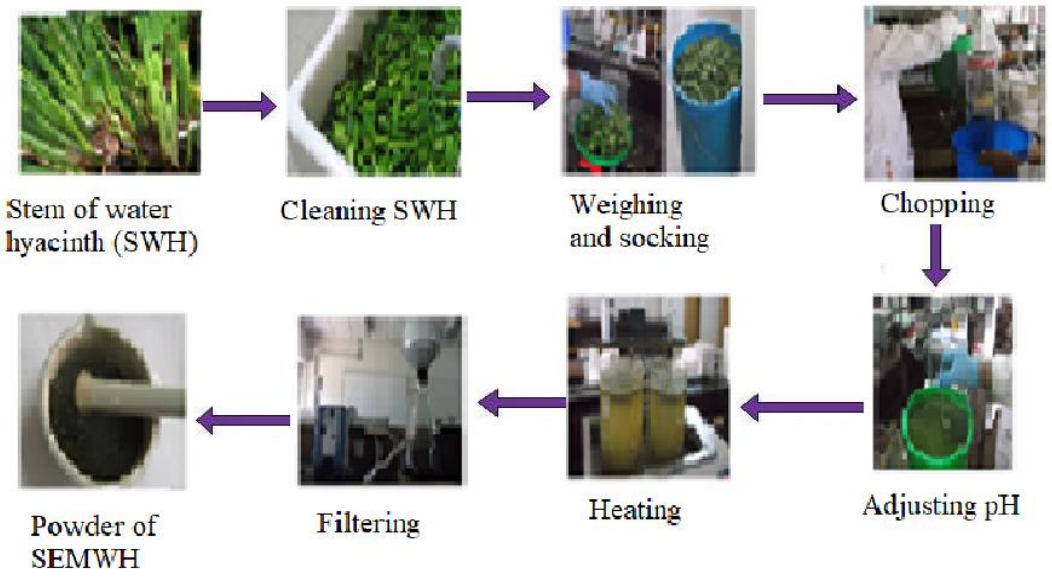

Figure 3. Schematic representation of the stem of water hyacinth sample preparation and extraction process for adsorbent preparation.

3.4.2. Modification of adsorbent material

The stem extract material from water hyacinth-grafted-polyaniline copolymer was synthesized by radical polymerization to improve the efficiency of the biosorption property of water hyacinth **[43]**. A solution of (SEMWH) was prepared by dissolving 1.0 g of SEMWH in 100 mL of a 1 M HCl solution, and 0.98 mL of aniline monomer was dissolved with 100 mL of 1 M HCl then added drop wise at room temperature to this SEMWH solution to keep the 1:1 M ratios between the two monomers. Ammonium persulfate (0.1 M) aqueous solution was prepared in a 1 M HCl solution and added drop wise into the SEMWH-aniline solution. The mixture was stirred overnight under nitrogen atmosphere and a crude product was obtained. The reaction mixture was neutralized with 1M NaOH solution. Finally, the product was washed with excess ethanol and acetone, and dried in vacuum at 40 ^{o}C produced the desired SEMWH-grafted- PANI copolymer.

3.4.3. Real sample digestion

In order to determine the level Cr(VI) in the real sample that was collected from Bahir Dar tannery and filtered through a Whatman No. 45 filter paper. The organic matter was destroyed according to the following procedure: 25 mL of sample was taken and mixed with 5 mL of a mixture of conc. H_2SO_4 and conc. HNO_3 (1:1). The solution was boiled on a hotplate at 120 ^oC until dense white fumes of SO_3 just appeared. Aliquots of 5 mL of concentrated HNO_3 were added and the heating was continued until the solution was clear and no brown fumes were observed. Then, the solution was also heated until to dryness and 15 mL of 0.5% v/v HNO_3 were added and boiled to dissolve the soluble salts. After cooling, the solution was transferred into a 50 mL volumetric flask and the volume was made up with 0.5% v/v HNO_3.

Digested sample solution was transferred into a conical flask then 3 drops of methyl red indicator and few drops of concentrated NH_4OH were added until the solution turned yellow in color. Few drops of 1:1 of H_2SO_4 with water was added until the solution turned acidic followed by additional 1 mL of 1:1 H_2SO_4. The volume of the solution was maintained nearly 50 mL, boiling chip was added and heated up to boiling. 1 mL of sodium azide (NaN_3) was added to the above solution and continued to boil for 1 minute after which color faded completely. After cooling the solution pH was adjusted using 0.1 M H_2SO_4. The samples were analyzed for Cr(VI) by the a UV-Vis spectrophotometer method using 1,5-diphenylcarbazide reagent (63 mg 1,5-diphenylcarbazide in 25 mL of acetone), which reacts with Cr(VI), forming a colored complex that absorbs at 540 nm **[44]**.

3.4.4. Synthetic wastewater sample

Synthetic wastewater sample was prepared using potassium dichromate ($K_2Cr_2O_7$) salt. Stock solution was prepared and serial dilution rule was applied for adsorption study.

3.5. Standard solution preparation

A stock solution of hexavalent chromium concentration (1000 mg/L) was prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 0.2 M H_2SO_4 then diluted to 1000 mL, and 0.2 M H_2SO_4 was also prepared by adding 11.22 mL of concentrated H_2SO_4 (95-97)% to 600 mL distilled water and leveled it to 1000 mL. After preparation of 1000 mg/L hexavalent chromium (Cr(VI)), high range standards (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and100) mg/L, and low range standards (0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.4, 3.2, 4.0 and 4.8) mg/L were prepared using serial dilution formula.

3.6. Instrumental methods

3.6.1. UV-Vis spectrophotometry

Agilent technologies Cary 60 UV-visible spectrophotometer with a 1 cm quartz cell was used for Cr(VI) measurements at λ = 540 nm. Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample moves from one energy state to another energy state. The principle of UV-visible spectroscopy is based on the absorption of ultraviolet light or visible light by chemical compounds at a given wavelength which provides quantitative and qualitative information in the production of distinct spectra **[45]**. Information may be obtained as transmittance, absorbance or reflectance of radiation.

3.6.2. Soxtec™ 8000

The Soxtec™ 8000 solvent extraction is used for the determination of crude fat or extractable matter in a very wide range of sample matrices with a specific solvent like n-Hexane. It performs the four extraction steps boiling, rinsing, solvent recovery and auto-shut down, fully unattended **[46]**. The Soxtec™ 8000 solvent extraction system is very fast, easy to operate and can analyze twelve samples within one hour. The sample to be analyzed is weighed into thimbles and inserted into the extraction unit and after completion of extraction the percent of crude fat is calculated as follows.

$$\% \text{ Crude fat} = \frac{(W1 - W2)}{SW} \times 100 \quad (1)$$

Where, W1, W2 and SW are weight of aluminum cap and crude fat after extraction, weight of empty aluminum cap and sample weight, respectively.

3.6.3. Fibertec ™ 8000

Fibertec™ 8000 auto fiber analysis system is used for the determination of crude fiber (CF), neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL). It is fast and easy to operate any fiber analysis system. Sample crucibles are handled separately used both as an integral part of the assembly during extraction, rinsing and filtration and as sample vessels during weighing, drying and ashing to determine crude fiber **[47]**. The percentage of crude fiber is calculated using equation (2).

$$\% \text{ Crude fiber} = \frac{W2 - (W3 + C)}{W1} \times 100 \quad (2)$$

Where, W_1 is weight of sample, W_2 is weight of (crucible + residue), W_3 is weight of (crucible + ash residue) and C is blank.

3.6.4. Fourier-transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy is one of the most important instrumental method which is used to characterize the functional groups of organic or inorganic compounds based on the molecular bonds vibration at several specific frequencies or wavenumber range. Fourier transform infrared spectroscopy has several advantages than other instrumental methods. This method or technique is non-destructive, high sensitive, fast, simple measurement mode, customizable workspaces, environmentally safe, and can be used for quantitative and qualitative analysis **[48]**. FT-IR spectroscopy is the observation of how light is scattered or absorbed upon reaching a solid, liquid or gas material.

3.7. Adsorption study

3.7.1. Adsorption isotherms and kinetics study

All batch adsorption studies were carried out at room temperature (22 $\pm$ 2 ^{o}C) using 10 mL of a Cr(VI) ion solution and shaked at constant speed using KS oscillator. The pH (1, 2, 3, 4, 5 and 6) of the experimental solutions were adjusted to the desired pH by drop wise addition of 0.1 M H_2SO_4 and 0.1 M NaOH to the ion solutions with stirring and monitoring by a Benchtop pH meter, which was calibrated using pH 4.0 and 7.0 buffer solutions. For the equilibrium isotherm study, 5 mg of stem extract material from water hyacinth adsorbent was mixed with 10 mL of (0.5, 1, 2, 4, 5, 6, 8, 10, 12, 14 and 16) mg/L initial concentration of hexavalent chromium solutions at pH 1 and shaked for 240 min.

For the adsorption kinetics study, 5 mg of stem extracted material from water hyacinth was added to the adsorbate solution with initial concentration of 5 mg/L in the time intervals (5, 10, 15, 20, 30, 60, 90, 120,150, 180,210, 240,270, 300 and 360 min). The concentration of Cr(VI) was measured using UV-vis spectroscopy at 540 nm wavelength for low range initial concentrations. The effects of pH (1, 2, 3, 4, 5 and 6) and adsorbent dose (0.5, 1, 2, 3, 4, 5, 6, 7, 8 and 9 mg) on the adsorption behavior were studied. For each measurement, three replicates were performed and averaged.

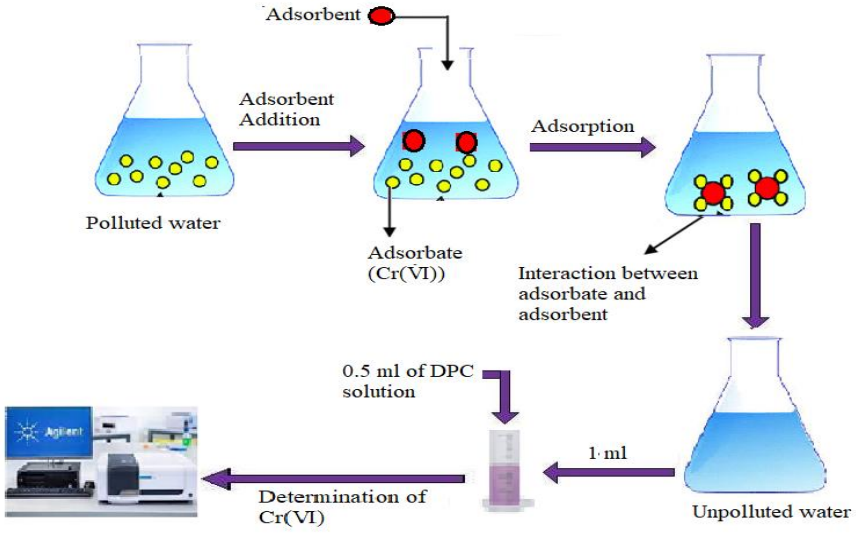

Figure 4. Adsorption process for the removal of Cr(VI) from tannery wastewater or polluted water.

The equilibrium adsorption capacity and the percent removal (%R) of Cr(VI) was calculated using equations (3) and (4).

$$q_e = \frac{(Co-Ce)V}{m} \quad (3)$$

$$\%R = \frac{(Co-Ce)100}{Co} \quad (4)$$

Where q_e (mg/g) is the adsorption capacity of adsorbent for Cr(VI), C_0 and C_e (mg/L) are the liquid phase concentrations of Cr(VI) before and after adsorption, respectively. V (L) and m (g) are the volume of the adsorption solution and the mass of the dry adsorbent used, respectively.

An adsorption isotherm is a function of the metal ion concentrations or materials in (mol m^{-2} or mg m^{-2}) adsorbed on a substrate (solid, liquid, or gas) at room temperature. The obtained results were tested with the two well-known models that are Langmuir and Freundlich models. In Langmuir isotherm model, adsorption occurs at specific sites on the adsorbent and adsorption energy has been homogeneously distributed on the absorbent surface **[49]**. The fundamental characteristics of Langmuir isotherm can be expressed by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{KLq_m} + \frac{C_e}{q_m} \quad (5)$$

$$q_e = \frac{q_m KLC_e}{1 + KLC_e} \quad (6)$$

$$R_L = \frac{1}{1+KLC_O} \quad (7)$$

Where C_e and q_e equilibrium concentration and adsorption capacity, respectively, q_m is the maximum monolayer adsorption capacity of the adsorbent, K_L (L/mg) is the Langmuir constant describing adsorption affinity for the adsorbent. The value of R_L indicates the type of the isotherm to be either; unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$).

The Freundlich isotherm model is suitable for adsorption processes occurring on heterogeneous surfaces. Heterogeneous distribution of active sites and also multilayer adsorption are assumptions of Freundlich isotherm. Freundlich isotherm is a mathematical expression for the adsorption equilibrium between a fluid (liquid or gas) and a solid material and the equation is represented by Eq. (8) and Eq. (9) for nonlinear and linear, respectively.

$$q_e = K_F C_e^{1/n} \tag{8}$$

The equation can be linearized and temperature dependent constants K_F and 1/n are obtained by linear regression:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \tag{9}$$

K_F (mg/g) (L/mg) $^{1/n}$ is the Freundlich constant related to the multilayer adsorption capacity and n is the heterogeneity factor, which represents the extent to which the adsorption depends on the equilibrium concentration. If l/n = 0, it means irreversibility; if 0 < 1/n < 1, it means desirability; and if 1/n > 1, it means undesirable isotherm.

Adsorption kinetics is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbents dose, flow rate and pH. In batch adsorption systems, several models describing the adsorption kinetics. However, PFO and PSO models have been widely used to describe the rate of adsorption in liquid -solid interactions. The data obtained from the kinetic tests are fitted to the PFO and PSO models, respectively. The kinetic model that fits to PFO reaction plot by giving R^2 value close to 1, it

indicates that the reaction is more inclined towards physisorption. Similarly if the reaction fits well to PSO model it indicates an inclination towards chemisorption. PFO equation (10) and PSO model, equation (11) assumes that the adsorption rate is based on the adsorption capacity.

$$\ln(q_e\text{-}q_t) = \ln q_e\text{-}k_1 t \quad (10)$$

Where q_t and q_e (mg/g) are the amount of hexavalent chromium adsorbed per mass of adsorbent (g) at time t (min) and at equilibrium, respectively, and k_1 (1/min) the rate constants of the pseudo-first-order.

$$q_t = \frac{q_e^2\, k_2 t}{1 + q_e t} \quad (11)$$

Where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and at any time t (min), respectively and K_2 (g/mg min) is the PSO equation rate constant.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (12)$$

The adsorption kinetics reflect the evolution of the adsorption process versus time and the adsorption process depends on the experimental parameters, such as pH, ionic strength, concentration of solute, adsorbent dose, the texture of adsorbents. Therefore, the contact time where the adsorption process approaches a true equilibrium must be determined according to these parameters.

3.8. Physico-chemical composition of the adsorbent

3.8.1. Moisture

Water occurs in any of the following form in the samples; adsorbed on the surface of the colloidal particles in cell constituents, water of hydration in chemical combination with various substance like carbohydrates and hydrates of salts.

Determination of the loss in mass on drying of the adsorbent material under a temperature of (130 ± 3^{o}C) gives a measure of moisture present in the adsorbent **[50]**.

$$\text{Moisture content (\%)} = \frac{(W1-W2)}{SW} \text{ x } 100 \qquad (13)$$

Where, W_1 is weight of sample and aluminum cup before drying, W_2 is weight of sample and aluminum cup after drying and S_W is weight of sample taken.

3.8.2. Ash

Ash refers to the remaining or residual parts mainly inorganic substances after the total incineration of organic matter. The ash content is determined from the loss of weight, which occur from complete oxidation of sample at a high temperature at 550^{o}C ± 3 ^{o}C through combustion and volatilization of organic materials of the adsorbent **[51]**.

$$\text{Ash content (\%)} = \frac{(W1-W2)}{SW} \text{x } 100 \qquad (14)$$

Where, W_1, W_2 and S_W are weight of ash and crucible, weight of empty crucible and weight of sample taken, respectively.

3.8.3. Fat

Fat is the extractable matter from extraction with a specific solvent like n-Hexane. Crude fat is a mixture of crude fat- soluble material in the sample which provides energy in the body. Fat is the main energy storage and gives important functions in the body. The amount of crude fat in the adsorbent material was determined using soxtec^{TM} 8000 solvent extraction system.

3.8.4. Protein

Proteins are made up of many building blocks, known as amino acids. Our body needs dietary protein to supply amino acids for the growth and maintenance of our cells and tissues. Proteins with large number of functional groups have a potential to remove heavy metals. The Kjeldahl method is used to determine the nitrogen content in organic and inorganic samples **[52]**.

Sample protein (-N) + H_2SO_4 $\xrightarrow{\text{catalyst}}$ $(HN_4)_2SO_4 + CO_2 + H_2O$

Protein (%) = Nitrogen (%) x 6.25 (15)

3.8.5. Fiber

Fiber (roughage) is the part of plant-based food such as grains, fruits, vegetables, nuts and beans that the body cannot break down. It passes through the body undigested, keeping the digestive system clean and healthy, easing bowel movements, and flushing cholesterol and harmful carcinogens out of the body. The crude fiber of the adsorbent material was analyzed using fibertec™ 8000 auto fiber analysis system.

4. Results and Discussion

4.1. Physico-chemical analysis of the adsorbent

The result of physico chemical analysis of SEMWH is presented in **Table 3**. Protein and fat were found to be the chief composition in SEMWH. SEMWH has also a good nutritional value of ash and moisture contents. The percentage composition of fat in SEMWH was found to be higher than that of fiber and less than protein. The presence of crude protein, crude fat and crude fiber indicates the adsorbent material can adsorbs the metal ions on the surface of it.

Table 3. Physico-chemical composition of the adsorbent material.

Composition	Concentration (%)
Crud fiber	2.21 $\pm$ 0.34
Crude fat	10.1 $\pm$ 0.20
Crude protein	32.5 $\pm$ 0.25
Moisture	6.50 $\pm$ 0.40
Ash	21.6 $\pm$ 0.30

4.2. FT-IR Study

The functional groups that are responsible for adsorption present in the SEMWH and SEMWH-AN of the pure adsorbents and chromium-loaded adsorbent samples were measured on spectrum 65 FT-IR (PerkinElmer) in the range 4000-400 cm^{-1} (resolution: 4 cm^{-1}, number of scans: 4) using KBr pellets.

The FT-IR spectra in **Figure 5** exhibit a number of absorption peaks, due to the nature of adsorbent examined before and after adsorption of chromium. The functional groups of the adsorbent can be characterized and identified by the steepness of the peaks.

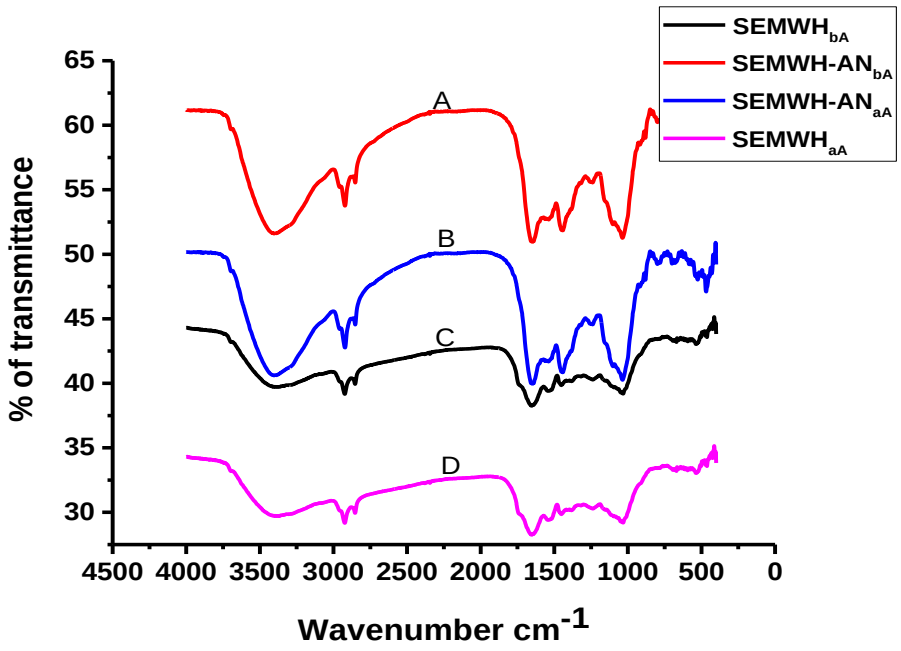

Figure 5. FT-IR spectra of the stem extract material from water hyacinth: (A) SEMWH-ANbA, (B) SEMWH-ANaA, (C) SEMWHbA and (D) SEMWHaA.

The FT-IR spectra of both SEMWH and SEMWH-AN before and after adsorption of Cr(VI) are shown **Figure 5**. The FT-IR absorption bands of SEMWH-AN in **Figure 5**A and B were obtained at 3400, 3344, 2924, 1650, 1314, 1124, 1027 and 530 cm^{-1}. The peak at 3400 and 3344 indicate broad band due to amine group stretching vibrations **[53]**. The peak at 2924 cm^{-1} indicates C-H stretching band. The absorption at 1650 cm^{-1} was due to C=O stretching, and the CH_2 wagging and the C-O stretching are assigned 1314 cm^{-1}. Absorption peak at 1124 cm^{-1} indicates the carboxyl groups **[54]**.

Absorption band around 1027 cm^{-1} represents C-H out of plane deformation vibration and the bands at 530 cm^{-1} C-H out of plane bending. The absorption peaks for SEMWH in **Figure 5** C and D were at wavenumbers of 2924, 1655, 1314, 1020 and 527 cm^{-1}. The peak at around 2924 cm^{-1} indicates presence of functional group C-H stretch and the peaks at 1655 cm^{-1} represents C=O. The peaks at 1314 cm^{-1} and 1020 cm^{-1} correspond to C-N stretching and C-H out of plane, respectively. Peak at around 527 cm^{-1} indicates that, there is C-H out of plane bending. In both cases, the decrease in percent of transmittance and wavenumber could be due to the higher steric hindrance for the formation of hexavalent chromium complexes on positively charged groups of the SEMWH and SEMWH-AN adsorbents **[55]**.

4.3. Analysis of hexavalent chromium standard calibrations

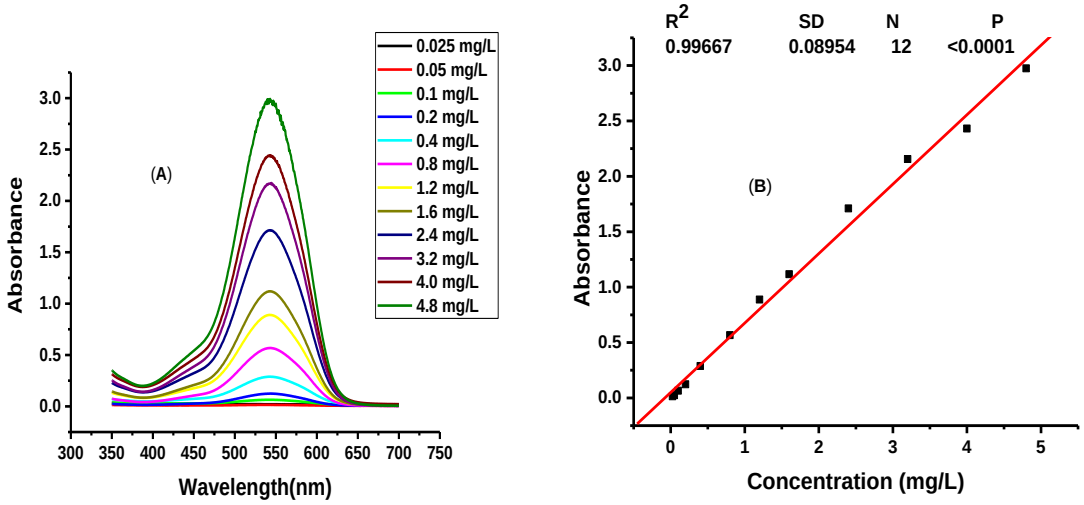

Figure 6. (A) Represents the spectra and (B) standard calibration curve of low range concentrations.

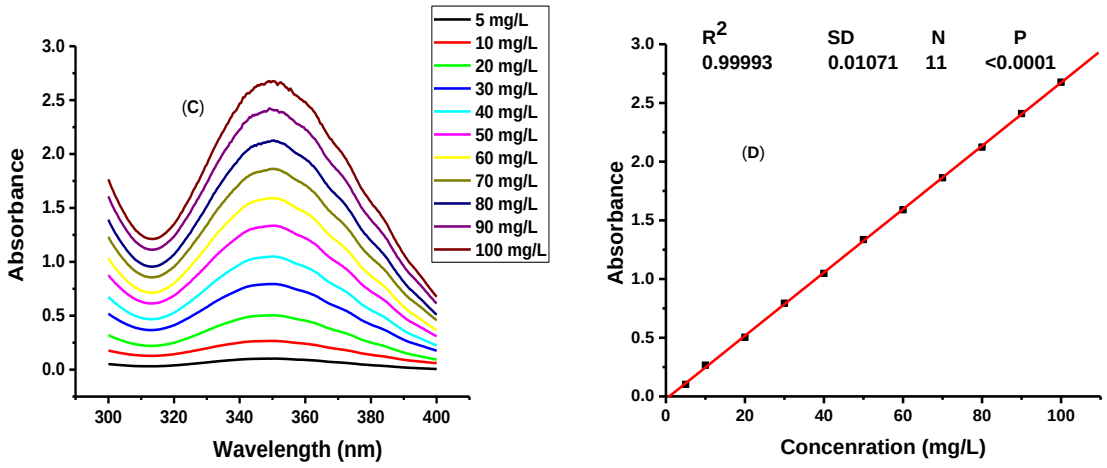

Figure 7. (C) Represents the spectra and (D) standard calibration curve of high range concentrations.

Low and high range standards were measured using UV-Vis spectroscopy at 540 and 350 nm wavelength, respectively. The calibration curve and correlation coefficient of hexavalent chromium was determined by plotting absorbance versus working standard concentrations. The correlation coefficient of hexavalent chromium for low range and high range standards were found to be 0.99667 and 0.99993, respectively.

4.4. Optimization of the adsorption studies

4.4.1. Effect of pH

The effect of pH on the adsorption of hexavalent chromium was studied at different pH (1.0-6.0). The pH of the solution affects the adsorbent properties such as surface charge, adsorbate speciation and degree of ionization in aqueous solutions. In aqueous solutions, Cr(VI) exist in several stable forms such as, $HCrO_4^-$, $HCr_2O_7^-$, H_2CrO_4 (pH < 2), $Cr_2O_7^{2-}$ and CrO_4^{2-} (pH 2–6) depending upon the pH of the solution **[56]**.

Figure 8 summarizes the effect of pH on hexavalent chromium (Cr(VI)) removal by SEMWH and SEMWH-AN. The optimum pH for the maximum removal percentage of Cr(VI) was found to be pH 1.0. The removal percentages of Cr(VI) were 67.84% and 76.90% on the SEMWH and SEMWH-AN adsorbents, respectively. At lower pH there is a strong electrostatic attraction between the positively charged surfaces of adsorbent and Cr(VI) ions **[57]**. When the pH increased, the surface of adsorbent becomes negatively charged due to deprotonation of functional groups on the adsorbent surface. As a result, there is an electrostatic repulsion between the adsorbent and the anion forms of Cr(VI) which leads to decrease the extent of adsorption process.

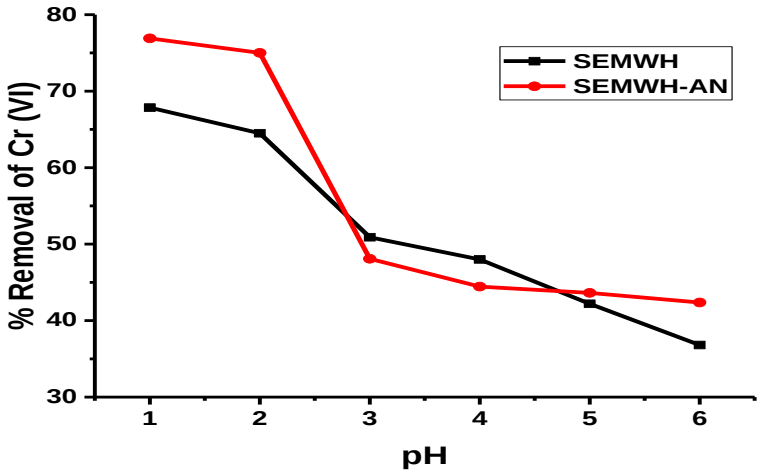

Figure 8. Graphical illustration of the effect of pH on the percent removal of hexavalent chromium by SEMWH and SEMWH-AN. Experimental conditions: adsorbent dose 5 mg, volume 10 mL, contact time 120 min and temperature 22 ± 2 °C.

4.4.2. Effect of contact time

The effect of contact times (5-360 min) on the batch adsorption process at temperature of 22 ± 2 °C, adsorbent dose (5 mg), 10 mL of volume and pH (1) were studied. **Figure 9** and **Figure 10** show the effect of contact time on the removal percentages of Cr(VI) and the adsorption capacities, respectively. The adsorption capacities and the removal percentages of Cr(VI) increased with time in the first stage of adsorption process and reached maximum removal percentage (96.0% for SEMWH and 99.9% for SEMWH-AN adsorbents) at equilibrium time of 240 and 210 min, respectively. This is attributed to high availability of vacant adsorption sites in the first stage of adsorption. As time increases removal percentage and adsorption capacity becomes constant due to the repulsive forces of the adsorbed ions and the difficulty to access the active sites **[58]**.

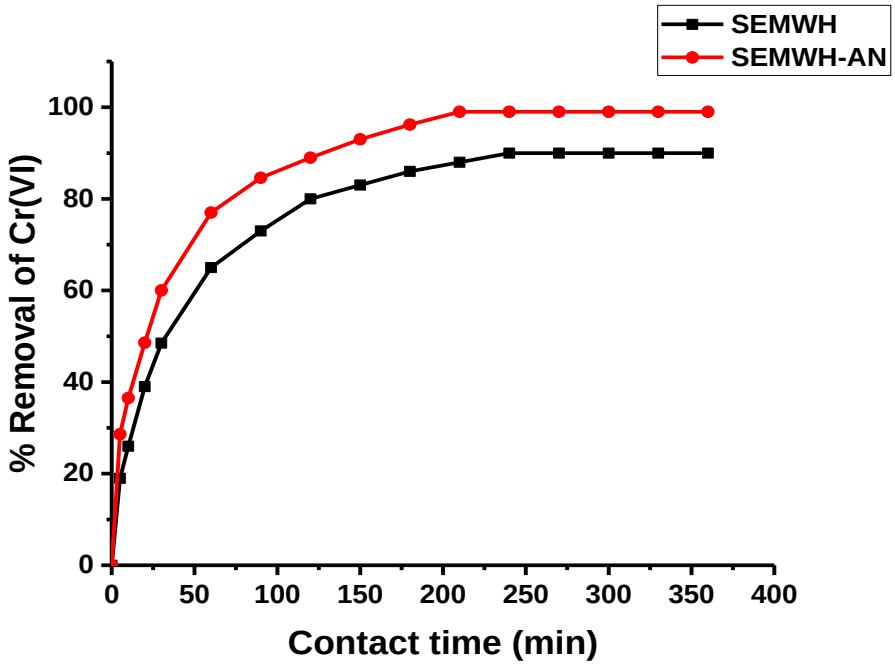

Figure 9. Removal percentage of hexavalent chromium by (SEMWH) and (SEMWH-AN). Experimental conditions: adsorbent dose 5 mg/ 10 mL, pH 1 and temperature 22 ± 2 °C.

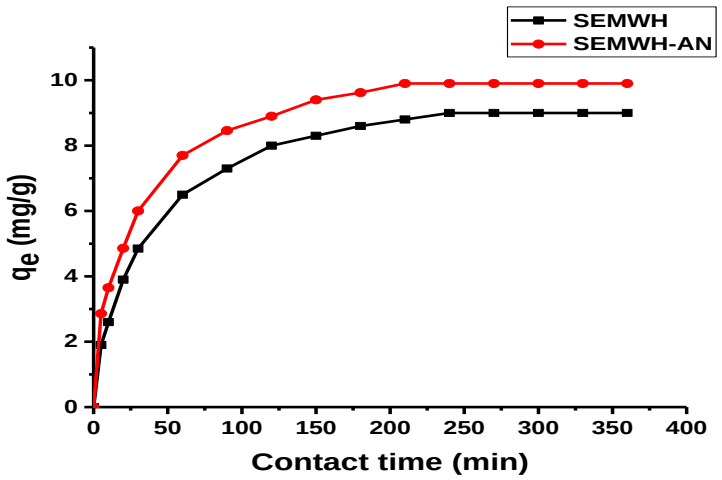

Figure 10. Adsorption capacity of hexavalent chromium by SEMWH and SEMWH-AN. Experimental conditions: adsorbent dose 5 mg/ 10 mL, pH 1 and temperature 22 ± 2 °C.

Figure 11 shows the adsorption capacities of the adsorbent materials with respect to equilibrium concentrations of the hexavalent chromium. The adsorption capacity of hexavalent chromium on SEMWH-AN is better than SEMWH due to the presence of aniline.

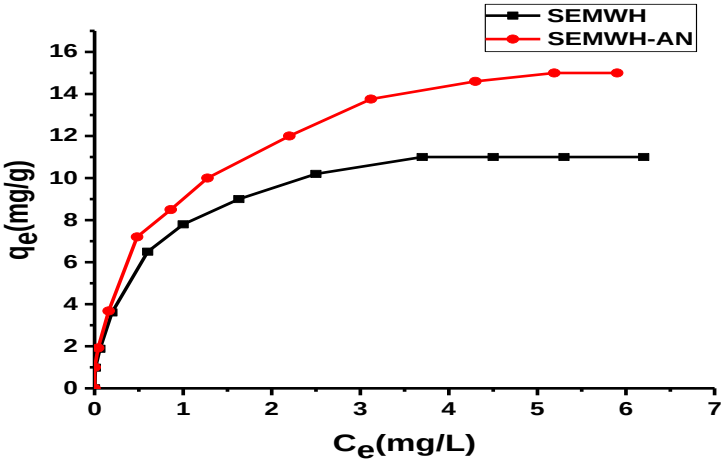

Figure 11. Absorption capacity vs equilibrium concentration of hexavalent chromium by SEMWH and SEMWH-AN. Experimental conditions: adsorbent dose 5 mg/ 10 mL, pH 1 contact time 240 and 210 min.

4.4.3. Effect of initial concentration

The Cr(VI) solutions of different concentrations (0.5, 1, 2, 4, 5, 6, 8, 10, 12, 14 and 16) mg/L were studied at pH 1, constant agitation speed, contact time 240 min for SEMWH and 210 min for SEMWH-AN, and the adsorbent dose 0.5 g/L as shown in **Figure 12** and **13**. The removal percentages of Cr(VI) were slightly reduced, and the adsorption capacities of Cr(VI) were increased for both SEMWH and SEMWH-AN adsorbents with an increase in initial concentration of Cr(VI) and becomes constant after equilibrium time. This behavior could be ascribed to the presence of a higher concentration of adsorbate per unit mass of adsorbent and which may restrict adsorption because, initial concentration provides a significant driving force to overcome all mass transfer resistance of metal ions between aqueous and solid phases **[59]**. Therefore, at low concentration, the binding sites took up the available ions quickly, but at higher concentration, the adsorption species needed to diffuse to the internal sites by intra-particle diffusion, resulting in reduced adsorption rate.

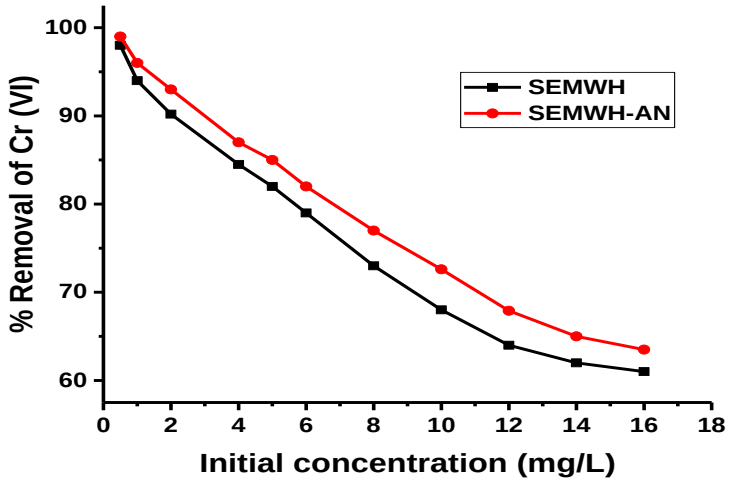

Figure 12. Effect of initial concentration on the removal percentage of hexavalent chromium by SEMWH and SEMWH-AN.

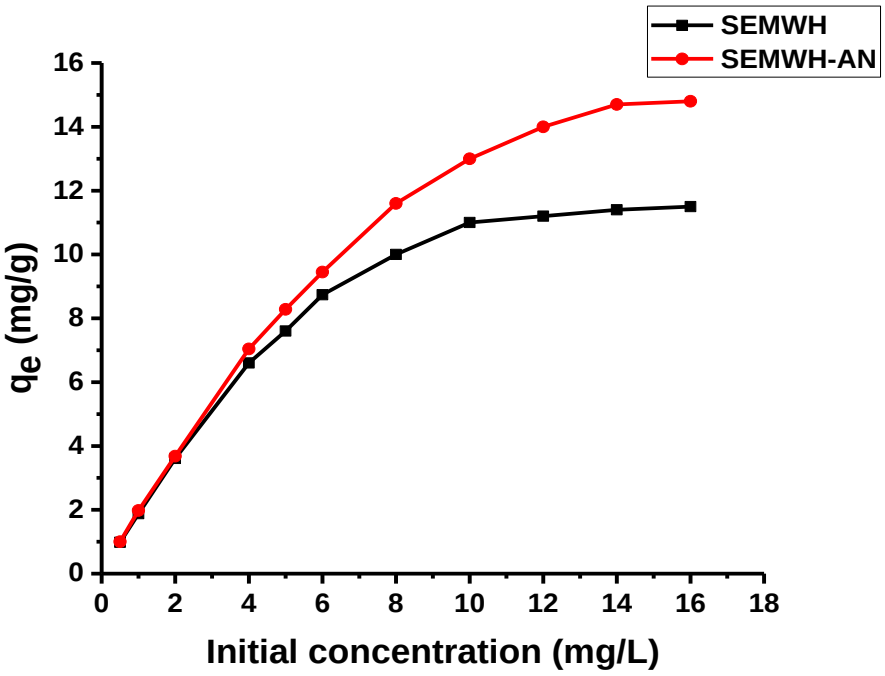

Figure 13. Effect of initial concentration on the adsorption capacity of hexavalent chromium by SEMWH and SEMWH-AN.

4.4.4. Effect of adsorbent dosage

Figure 14 and **15** show the effect of adsorbent dosage on the removal percentages of hexavalent chromium and the adsorption capacities of adsorbents. The removal percentages of hexavalent chromium increased (20 to 85.5% and 33 to 99.9%) for SEMWH and SEMWH-AN as adsorbents dosage increases from (0.5 mg/10 mL to 5 mg/10 mL), respectively. The adsorption capacities decreased from 20 to 8.40 for SEMWH and 33 to 9.87 for SEMWH–AN adsorbents due to the fact that all active sites were entirely exposed at lower doses, while only a fraction of the active sites were exposed at higher doses **[60]**. Thus, a higher adsorbent dosage may cause aggregation and which decreases the total surface area of adsorbent leading to a decrease in adsorption **[61]**.

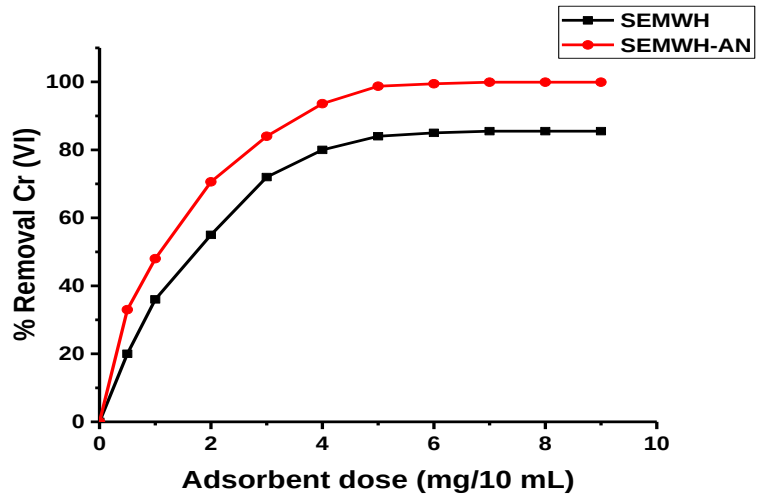

Figure 14. Removal percentage of hexavalent chromium by SEMWH and SEMWH-AN. Experimental conditions: at different dose, initial concentration 5 mg/L, pH 1 and temperature 22 ± 2 °C.

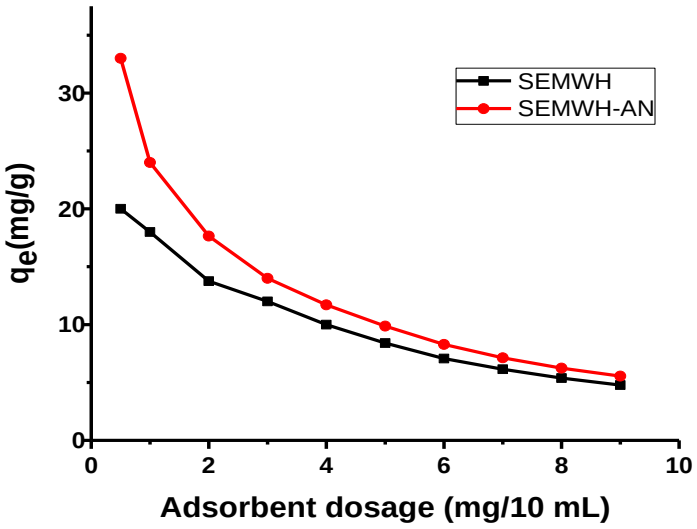

Figure 15. Adsorption capacities of hexavalent chromium on SEMWH and SEMWH-AN. Experimental conditions: at different dose, initial concentration 5 mg/L, pH 1 and temperature 22 ± 2 °C.

4.5. Adsorption isotherm models

The adsorption isotherms describe the distribution of adsorbed molecules between the solid and liquid phase when the adsorption reaches at equilibrium. Langmuir and Freundlich models are well-known adsorption isotherm models. The linear form of the two models were applied for calculation and the corresponding parameters are given in **Table 4**. The adsorption isotherm model of the experiment followed Langmuir model, which indicates the adsorption process was onto homogeneous surfaces and that exhibits one type of adsorption site **[49]**. The adsorption capacities corresponding to the monolayer adsorption were found to be 31.8 for SEMWH and 35.6 mg/g for SEMWH-AN adsorbents. The obtained R_L value of 0.35 and 0.29 suggested favorable adsorption of Cr(VI) onto SEMWH and SEMWH-AN, respectively.

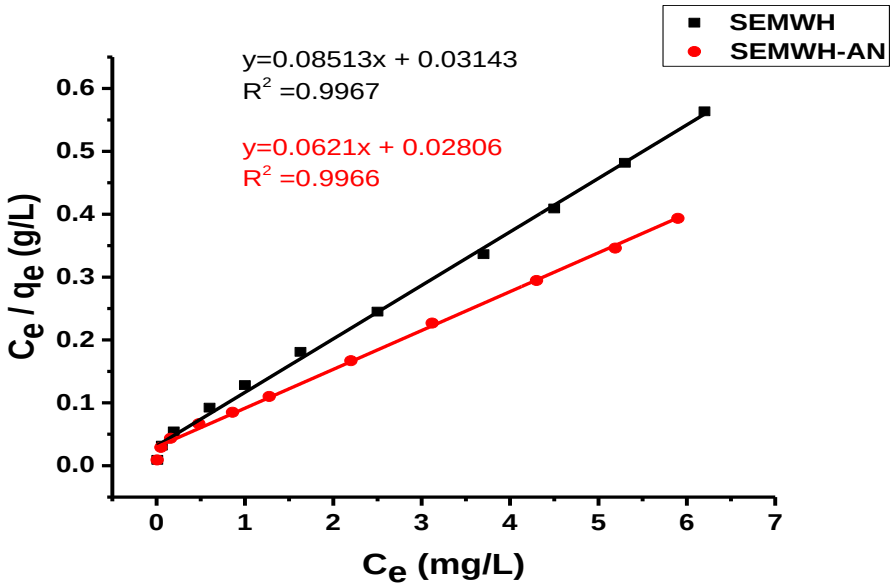

Figure 16. Langmuir model of Cr(VI) adsorption on SEMWH and SEMWH-AN at 5 mg/L. Experimental conditions: adsorbent dose 5 mg/10 mL, pH 1.0 and temperature 22 ± 2 °C.

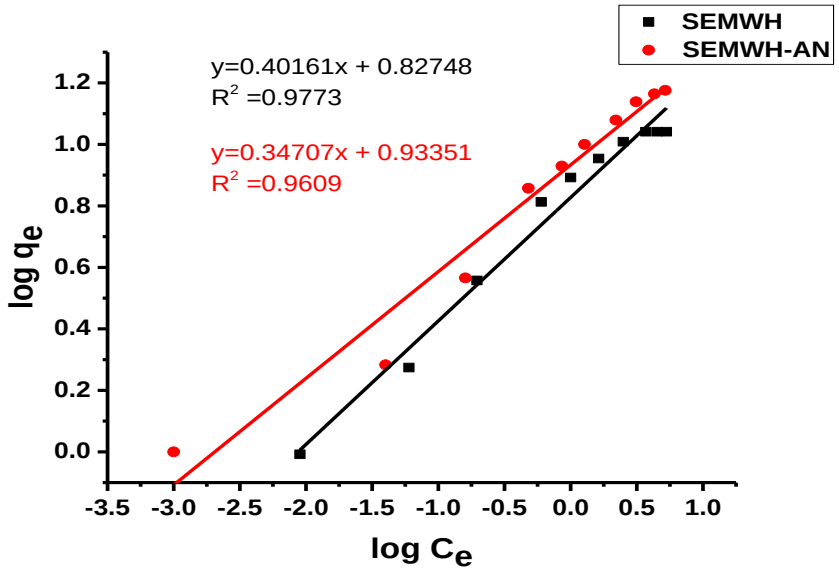

Figure 17. Freundlich model (log qe vs log ce) of Cr(VI) adsorption on SEMWH and SEMWH-AN at 5 mg/L. Experimental conditions: at adsorbent dose 5 mg, volume of solution 10 mL, pH 1.0 and temperature 22 ± 2 °C.

Table 4. Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption on SEMWH and SEMWH-AN adsorbents.

Adsorbent	Langmuir				Freundlich			
	q_m (mg/g)	K_L (L/mg)	R^2	R_L	1/n	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
SEMWH	31.8	0.37	0.9967	0.35	0.40	2.49	6.72	0.9773
SEMWH-AN	35.6	0.48	0.9956	0.29	0.35	2.88	8.58	0.9609

4.6. Adsorption kinetics models

Pseudo-first and pseudo-second-order kinetics models are shown in **Figures 18** and **19**, and the calculated kinetic parameters are illustrated in **Table 5**. The higher correlation coefficient (R^2) values obtained from the pseudo-second-order (0.9989 and 0.9991) compared to those of the pseudo-first-order (0.9150 and 0.9514) kinetic model for the SEMWH and SEMWH-AN adsorbents, respectively. The adsorption more closely followed the pseudo-second-order kinetics which is chemisorption. In addition, the adsorption capacities calculated from the pseudo-second-order model agreed with the experimental values.

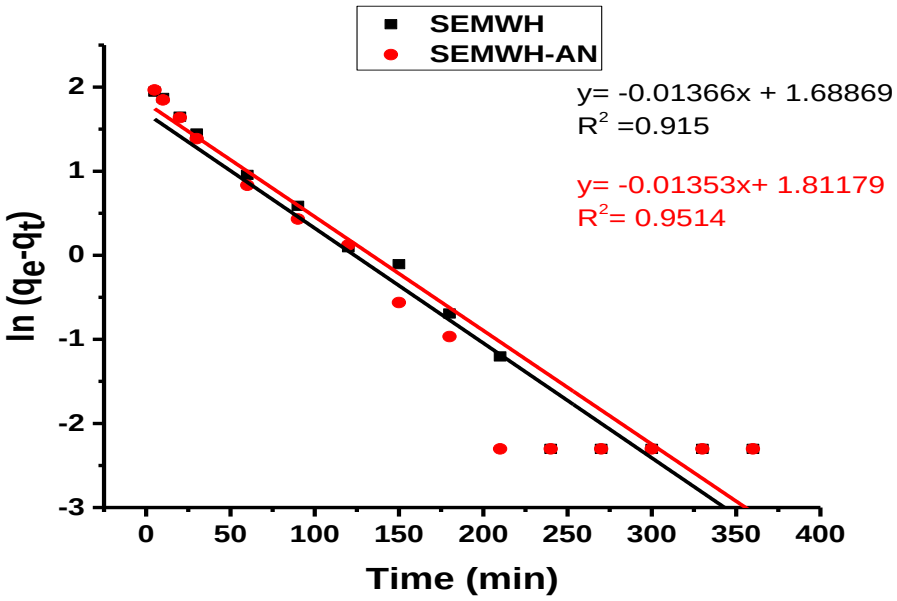

Figure 18. Pseudo-first-order kinetic of Cr(VI) adsorption on SEMWH and SEMWH-AN at 5 mg/L. Experimental conditions: adsorbent dose 5 mg/10 mL, pH 1.0 and temperature 22 ± 2 °C.

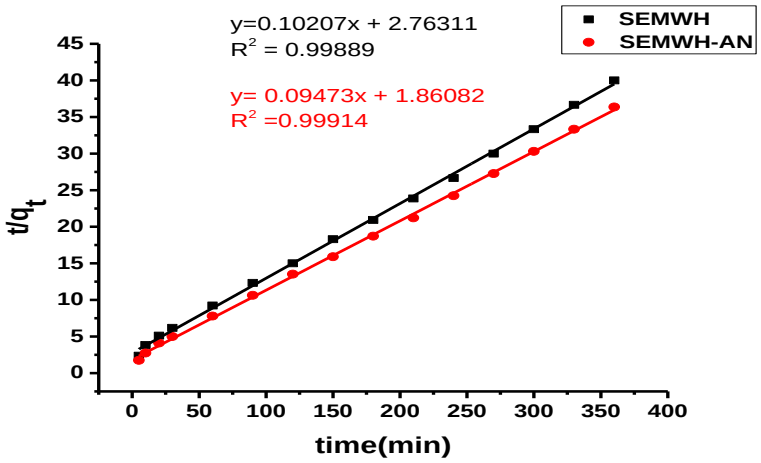

Figure 19. Pseudo-second-order kinetic of Cr(VI) adsorption on SEMWH and SEMWH-AN at 5 mg/L. Experimental conditions: adsorbent dose 5 mg/10 mL, pH 1.0 and temperature 22 ± 2 °C.

Table 5. Kinetic parameters of pseudo-first-order and pseudo-second-order equations for Cr(VI) adsorption on SEMWH and SEMWH-AN, at Co = 5 mg/L.

Adsorbents	q_e-expt (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/(mg.min))	R^2
SEMWH	9.00	5.41	$5.7x10^{-5}$	0.9150	9.79	$3.8x10^{-3}$	0.9989
SEMWH-AN	9.90	6.12	$5.6x10^{-5}$	0.9514	10.56	$4.8x10^{-3}$	0.9991

4.7. Analysis of real sample and synthetic wastewater

Stem extract material from water hyacinth and its modification with aniline adsorbents were used to remove hexavalent chromium from real sample. **Table 6** shows the obtained results in tannery wastewater were 0.170 mg/L, 0.001 and 0.59 for mean, standard deviation and percent of relative standard deviation, respectively, that is above permissible limits of EPA and WHO. The data was analyzed using **Minitab 17** software. Minitab is the statistical software that helps in taking out the complexities of statistical calculations because it is easy to use, to calculate and draw various graphs.

Table 6. Summary of the mean Cr(VI) concentration in wastewater samples collected from Bahir Dar tannery.

Sample	N	Cr(VI) in (mg/L)	SD	%RSD	SE Mean	SS	MS	F_{expt}	F_{crit}	P
WWS1		0.170	0.001	0.59	$5.8x10^{-4}$	$5x10^{-7}$	$5x10^{-7}$	0. 33	6.61	0.67
WWS2		0.169	0.001	0.59	$5.8x10^{-4}$	$1.5x10^{-6}$	$1.5x10^{-6}$			

N indicates the number of triplicate trials.

The obtained P–value (0.67) is greater than 0.05 within 95% confidence level, which doesn't show statistically significant difference between wastewater samples (WWS1 and WWS2), and indicates strong evidence for the null hypothesis. This means retain the null hypothesis and reject the alternative hypothesis. The value of F_{expt} (0.33) is less than F_{crit} (6.61) which also indicates that

there is no significant difference between the two wastewater samples, but the values of the two samples are not exactly the same due to random error.

4.8. Removal of hexavalent chromium from wastewater

SEMWH and SEMWH-AN were used as an adsorbent material for the removal of chromium from the wastewater. **Figure 20** shows that the removal of Cr(VI) ions from the collected wastewater sample by using SEMWH and SEMWH-AN adsorbents. The removal of Cr(VI) ions from real sample achieve WHO permissible limit (0.05 mg/L) at a time of 15 min for SEMWH-AN and 18 min for SEMWH adsorbents. These results indicated that SEMWH and SEMWH-AN were efficient for the removal of Cr(VI) ions from wastewater. **Figure 21** and **22** show the removal total chromium from the real sample and synthetic wastewater sample using SEMWH and SEMWH-AH. The removal of Cr(VI) from real sample and synthetic wastewater using SEMWH-AN took 15 and 13 min, respectively, to achieve WHO permissible limit. While using SEMWH, the removal of Cr(VI) from real sample took 18 min and from synthetic wastewater took 15 min to achieve WHO permissible limit. The results obtained in both adsorbents were in good agreement for the removal of Cr(VI) from synthetic wastewater and real sample.

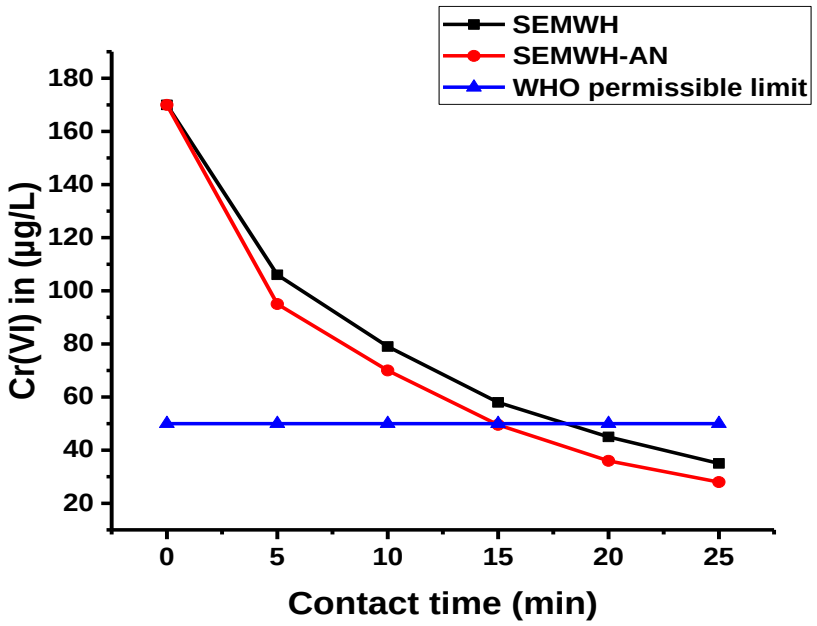

Figure 20. Concentration-time profile for the removal of 170 µg/L of Cr(VI) ions from the collected tannery wastewater sample by using SEMWH and SEMWH-AN adsorbents.

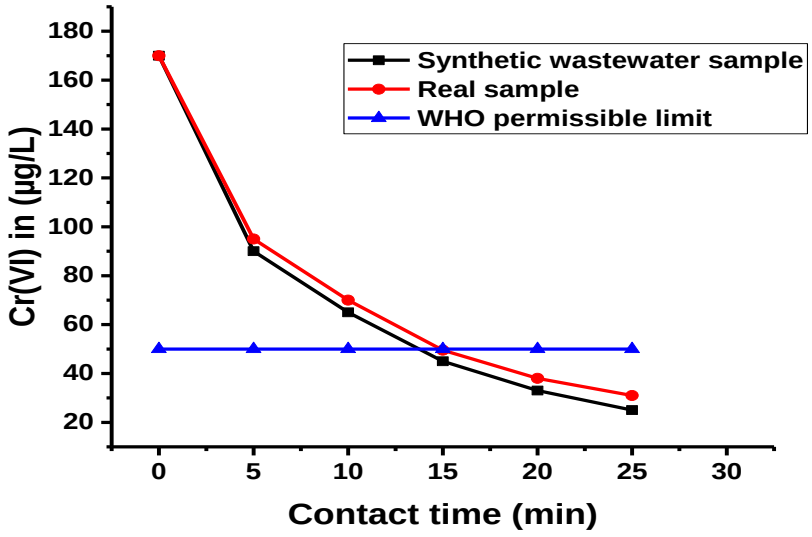

Figure 21. The effect of time on the removal of 170 µg/L of Cr(VI) ions from the collected tannery wastewater and synthetic wastewater sample by using SEMWH-AN.

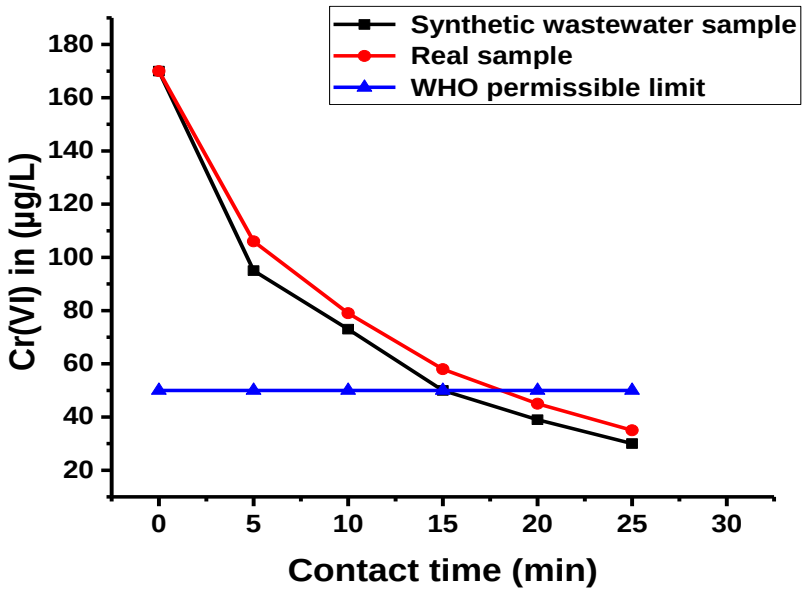

Figure 22. The effect of time on the removal of 170 µg/L of Cr(VI) ions from the collected tannery wastewater and synthetic wastewater sample by using SEMWH.

4.9. Comparison of the adsorption capacity and removal percentage of the adsorbent with literature

The adsorption capacity and removal efficiencies of other adsorbents for Cr(VI) ion taken from the literature are given in **Table 7** for comparison. The maximum adsorption capacities and removal percentages of Cr(VI) under this study were better than other literature values. Low cost and easily available adsorbent materials are selected for comparison. The adsorption capacity and removal percentage of those adsorbents varies between 1.28 and 39.06 (mg/g), and 92.39 and 99.90%, respectively.

Table 7. Comparison of the adsorption capacity and removal percentage of different adsorbents for Cr(VI).

Bio-sorbent Source	q_m (mg/g)	Adsorption Conditions				References
		pH	Adsorbent Dosage (g/L)	Contact time (min)	%R	
DWHR	1.28	3.00	5.00	100	-	**[29]**
Grapefruit	39.1	5.50	1.00	400	99.95	**[30]**
Pineapple core	8.80	2.00	30.0	1440	92.4	**[31]**
CSCS	9.43	2.00	1.00	140	94.0	**[32]**
Litchi peel	7.05	1.00	8.00	100	99.9	**[33]**
GBPs	6.17	3.00	4.00	120	96.0	**[34]**
SEMWH	31.8	1.00	0.50	240	96.0	**This work**
SEMHW-AN	35.6	1.00	0.50	210	99.9	**This work**

5. Conclusion

The stem extract material from water hyacinth has demonstrated as an alternative adsorbent material for the adsorption of hexavalent chromium. The adsorption capacities of Cr(VI) were found to be 31.82 and 35.64 mg/g for SEMWH and SEMWH-AN adsorbents, respectively. The adsorption capacity of the modified adsorbent (SEMWH-AN) has showed a twelve percent increment compared to that of the unmodified adsorbent (SEMWH). In addition, the maximum removal percentage of Cr(VI) was found to be 96.0% for SEMWH and 99.9% for SEMWH-AN. The adsorption kinetics more closely follows the pseudo-second-order kinetics which indicates that the adsorption process is chemisorption. The adsorption equilibrium obeys Langmuir isotherm which indicates that the adsorbent materials are monolayer. Compared to other adsorbent materials, the stem extract material from water hyacinth has demonstrated better adsorption capacity and removal percentage.

6. References

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