Addis Ababa University

College of Natural and Computational Sciences

Department of Chemistry

Removal of Cr(VI) by Adsorption using Milletta Ferruginea Seed Shell (MFSS)

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A thesis submitted to the department of Chemistry Addis Ababa University in partial Fulfilment of the requirements for the degree of Master of Science in Chemistry

August 2024

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 Department of Chemistry, Addis Ababa University.

The thesis "Removal of Cr(VI) by adsorption using *Milletia Ferruginea Seed Shell* (MFSS)" is conducted under the supervision of Dr Solomon Mehretie.

Department of Chemistry, Addis Ababa University, Ethiopia

Name Sintayehu Manahilot

Signature________________________

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

Advisor Name: Dr. Solomon Mehretie

Signature_____________________________

Place and date of submission: Natural and computational sciences.

Addis Ababa University

August 2024. E.C

Addis Ababa University

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Department of Chemistry

APPROVAL OF THE THESIS

Approved by the Examining committee:

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Dr. Solomon Mehretie (Advisor)	______________________	_______________
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Dr. Merid Tessema (Examiner)	______________________	_______________

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ABSTRACT

Wastewater treatment technologies for the removal of hexavalent chromium are currently one of the challenges in developing countries. An adsorbent prepared from *Millettia Ferruginea seed shell* (MFSS) was used to assess the adsorption of Cr(VI) ions from synthetic wastewater. Numerous factors, including pH, contact time, initial concentration, and dosage of the adsorbent, were optimized. The parameters for Cr(VI) adsorption on the adsorbent were 10 mg of adsorbent, pH 1 and 40 minutes of contact time. 10.55 mg/g was found to be the highest adsorption capacity, and at constant volume, the maximum percentage removal was 55.97%. The adsorption of Cr(VI) on the MFSS adsorbent was shown to obey pseudo-second order kinetics and to follow the Freundlich isotherm model.

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Abbreviations

BCF	**Bio concentration factor**
US EPA	**United States Environmental protection agency**
DNA	**Deoxyribonucleic acid**
MFSS	**Militia Ferruginous seed shell**
PFO	**Pseudo first order**
PSO	**Pseudo second order**
WHO	**World health organization**

1. Introduction

Environmental pollution is one of the major problems in the world due to industrial development or human activities to satisfy their needs. Significant amount of environmental pollutants mostly toxic heavy metals released from industries to the environment. The most familiar toxic pollutants are chromium, lead, cadmium, copper and mercury [1].

Hexavalent Chromium is one of the most toxic pollutants that have harmful effects on human health and aquatic lives [1, 2]. The toxicity of Cr(VI) leads to skin irritation, asthma, ulceration, severe diarrhoea, and harms the kidney, circulatory tissues, liver, and nerve tissues [2, 3]. Cr(VI) is released from industrial effluents in the process of electroplating, alloying, textile dying; leather tanning; metal polishing and pigment manufacture [4].

According to the world health organization (WHO) and United States Environmental protection Agency US (EPA), the tolerance limits for Cr(VI) in drinking and in land water, are 0.05 mg/L and 0.1 mg/L respectively [4,5]. Chromium is actually found in plants, rocks, soil, volcanic dust, animal and people. Cr(III) and Cr(VI) are found in natural water. Cr(III) is an essential micro nutrient for human and aquatic lives; it occurs naturally in the environment from the erosion of natural chromium deposits and also can be produced by industrial processes. Cr(VI) has negative effects on human beings and aquatic live, therefore it is essential to treat these effluents before discharging it into water bodies [5, 6].

There are several methods for the treatment of Cr(VI) bearing effluents, such as reduction, precipitation, electrochemical reduction, ion-exchange, reverse osmosis and adsorption. The above conventional methods require high capital and operating costs [6].

Adsorption is a process where collection of chemical substances at the surface of a solid material. The adsorption technique stays the most preferred procedure because of its low priced, efficiency, and non-hazardous technique. The substance adsorbed on the surface of another substance is an adsorbate, and substances which adsorb another substance on its surface are called an adsorbent [7, 8].

The effect of different parameters, such as pH, adsorbent dosage, concentration of Cr(VI) and contact time on the adsorption process have been studied [8].

Adsorption technologies with high performance, low cost and easy process control have great prospects for industrial wastewater treatment applications [9].

Environmental pollution due to the rapid growth of industries in the world result-in a large number of industrial wastewaters containing of heavy metals. Chromium is one of the top-heavy metals in wastewater; it has been broadly utilized in different mechanical forms. Cr(VI) is highly toxic than Cr(III) because it is soluble and can be easily absorbed and accumulate in the human, animal and plant bodies, mainly in human liver, stomach, and kidney. Therefore, it is necessary to remove Cr(VI) to acceptable levels before discharging it into water bodies [10].

Commonly contaminated wastewater with heavy metals effluent is untreated before discharging it into the environments, which become a serious problem for human health and aquatic life [10]. Currently urban agriculture is developing at a rapid rate to satisfy the need of the society for their food and nutrition.

The farmers in urban areas of developing countries including Ethiopia depend on wastewater sources to irrigate edible crops for urban markets. These edible crops accumulate heavy metals and that enter the food chain of animals and humans directly or indirectly. Thus, there should be a means of detoxification of these heavy metals from wastewater. This study focuses on the removal of hexavalent chromium from wastewater using locally available biomaterial namely MFSS- *berrebra.*

1.1. Objectives

1.1.1. General objective

The general objective of this research is to study the removal of Cr(VI) ion from industrial waste water by adsorption using *Millettia Ferruginea seed shell* (MFSS).

1.1.2. Specific objectives

1. To study the removal of Cr(VI) from industrial wastewater by adsorption process.

2. To study the effect of pH, adsorbent dose, contact time and initial concentration for the removal of Cr(VI) from industrial waste water.

3. To study the efficiency of the adsorbent for wastewater treatment.

2. Literature Review

2.1. Heavy metals

Heavy metals are elements which have high density and are toxic for humans, animals and organisms even at low concentrations. The most familiar toxic pollutants are chromium (Cr), lead (Pb), cadmium (Cd), copper (Cu) and mercury (Hg). Chromium is one of the most toxic metals that have toxic effects on human health [2].

Chromium is considered as toxic and usually found in the form of Cr(III) and Cr(VI).The literature showed that Cr(III) is an important nutrient for the metabolism of sugar and fat, and its toxicity is less than Cr(VI). Cr(VI) is highly toxic because it is highly soluble in water and can be easily absorbed directly or indirectly by human beings and aquatic lives [3].

2.2. Chromium

Chromium is a transition metallic element found in group VIB and period 4, with the symbol Cr atomic number 24 and atomic weight 51.996 g/mole, electron configuration $[Ar]4s^1 3d^5$,density 7.19 g/cm^3. Chromium is a naturally occurring element found in plants animals, rocks, soil, in volcanic dust and gases. Chromium is a hard metal, lustrous and silvery in colour and can be polished. The oxidation state of chromium is (-2 to + 6) state. The most important stable state is 0 in elemental states, +3 and +6 state exist in compounds. Cr(III) occurs in the environment and is an essential nutrient at low concentration, whereas Cr(VI) is produced by industrial process. Cr(III) and Cr(VI) occur in metallic or native chromium, chromate and dichromate compounds**.**

2.2.1. Sources of chromium

The chief ores of chromium in nature are chromite's (Cr_2O_3) and chrome ($FeOCr_2O_3$), which are used in the electroplating of metal to prevent corrosion, plastic coating of surfaces to prevent water and oil adverse effects, tanning leather, finishing metal, pigmenting and wood preservative; result in Cr(VI) bearing waste water discharge [13].

The primary sources of Cr(VI) in the atmosphere are chromate chemicals used as rust inhibitors in cooling towers and emitted as mists, particulate matter emitted during manufacture and use metal chromates, and chromic acid mist from the plating industry. Cr(VI) `may exist in aquatic media as water- soluble complex anions and may persist in water. Cr(VI) is a strong oxidizing agent and reacts with organic matter or other reducing agents to form trivalent chromium. Tanning industry is one of the sources of Cr(VI) in the -world.

The tanning industry uses chromium for converting raw materials or hides and skins in to leather for producing articles, like belt, bag, shoe, suitcase, wallet, and Jacket.

2.2.2. Chromium compounds

Cr(VI) species exist as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions. The chromate and dichromate ions are important in the preparation of industrial salts. Sodium dichromate ($Na_2Cr_2O_7$) and sodium chromate (Na_2CrO_4) are used in metal surface treatment, in leather tanning, and as catalysts in most industrial processes. Potassium dichromate ($K_2Cr_2O_7$), is used for an oxidizing agent for glass cleaning and chrome plating. Chromic acid (H_2CrO_4) is also used as analytical reagent in leather and tannery industry.

2.2.3. Uses of chromium and its compounds

Chromium is widely used in the metallurgical and chemical industries, in the production of stainless steel, alloy, cast iron, nonferrous alloys, plating steel for cars and bicycles, air craft, and is highly resistant to corrosion. Chromium is also used in the chemical industries as a Catalyst, petrochemical, and nuclear sectors for making steel, chrome plating, dyes and pigments, textile manufacturing, leather tanning and wood preserving.

Table1.Industrial uses of Cr(VI) compounds.

Name	Formula	Uses
Chromium oxide	Cr_2O_3	Used to make stainless steel and non- ferrous alloys or Super alloys
Barium chromate	$BaCrO_4$	Pyrotechnics, high temperature batteries
Cadmium chromate	$CdCrO_4$	Catalysts pigments
Cadmium dichromate	$CdCr_2O_7.H_2O$	Metal finishing
Calcium chromate	$CaCrO_4$	Corrosion inhibitors, high temperature batteries
Copper dichromate	$CuCr_2O_7.5H_2O$	Wood preservatives, catalysts
Magnesium chromate	$MgCrO_4.5H_2O$	Corrosion inhibitor in photo engineering, ceramics
Mercuric chromate	$HgCrO_4$	Antifouling formulation
Pyridine dichromate	$(C_5H_5NH)_2Cr_2O_7$	Photosensitize in photoengraving, ceramics
Strontium chromate	$SrCrO_4$	Corrosion inhibiting pigment, plating additive

2.2.4. Environmental and health impacts of chromium.

Water pollution due to release of industrial waste water is a serious problem for our environment. Cr(III)) and Cr(VI) are found in most industrial waste water. The toxicity of chromium depends on its oxidation states.

Chromium (VI) is more toxic than Cr(III) because Cr(VI) is more soluble and easily enter in to water, as it is taken by human beings, animals and aquatic life, it causes health problem.

According to the world health organization (WHO) and United state Environmental protection agency, US (EPA) the tolerance limit of Cr(VI) is 0.05 mg/L and 0.1 mg/L in drinking and in land surface waters respectively [4,16].

The bio-concentration factor (BCF) for Cr(VI) in fish muscle appears to be < 1.0 µg/L but values of 125 µg/L and 192µg/L were obtained for oyster and blue muscle respectively. Several case reports have been published on clinical signs and symptoms in individuals following acute accidental or international ingestion of high doses (fatal or near fatal) of Cr(VI) compounds, including chromic acid, potassium dichromate and ammonium dichromate. Clinical presentation of patients following acute, high dose exposure was similar, regardless of the specific Cr(VI) compound ingested, and included the following: abdominal pain, nausea, and vomiting; caustic burns of mouth, stomach, and duodenum, renal failure, cyanosis, and metabolic acidosis, hypotension and shock [15].

2.2.5. Removal of chromium (VI) by adsorption

In the present studies consideration has been made to prepare an adsorbent from *Milletia Ferruginea Seed Shell (MFSS*) for the removal of Cr(VI) from industrial waste water [8]. The discharge of untreated effluents coming from different industries lead ` to the contamination of natural- resources of soil and water [10, 11]

According to the world health organization (WHO) and the United state Environmental protection Agency US (EPA), Cr(VI) is considered as the known pollutant and must be eliminated or reduced using adsorption from contaminated water, which is released from industrial waste water [11].

Adsorption is a low-cost method and can remove up to 100% of Cr(VI) ion from aqueous solution. Based on the substance being deposited and adsorbed, adsorption is classified in to two types' physisorption and chemisorption [1, 2].

Physisorption is a physical adsorption process when an atom or molecule in the gas phase attaches to a solid surface due to a weak force (Vander Waals forces); whereas chemisorption is a chemical adsorption in which the adsorbed substance is held together by a chemical bond.

Table 2 . Comparison of physical and chemical adsorption.

	Physical adsorption	Chemical adsorption
Adsorption layer	Single or multiple	Single layer
Adsorption force	Van der Waals force	Chemical bond force
Adsorption rate	Fast	Slow
Selectivity	Non selective adsorption	Selective adsorption

Currently the discharge of Cr(VI) effluents in to water bodies affects aquatic animals, and human beings. Thus, the Cr(VI) ion should be removing before discharging in to the water system.

Table3.Some of health effects of Cr(VI) toxicity shown below.

Toxicity	Health effect	References
Toxicity and carcinogenicity	Damage the DNA, Genetic mutation	[11]
Carcinogenicity	Damage DNA and causes cancer	[12]
Respiratory Lung and nasal cancer	Lung and nasal cancer are associated with the exposure through inhalation and ingestion of drinking water	[13]
Reproductive and development.	Birth defect and decreased spermatogenesis	[18,19]

3. Materials and Methods

The experiments were conducted with aqueous solution of Cr(VI) by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) in distilled water.

3.1. Experimental studies

The studies were carried out in the physical chemistry laboratory of Addis Ababa University Arat Killo College of natural sciences, Department of chemistry. To determine optimum dose of *Millettia Ferruginea seed shell (MFSS)*, 10 ml of 30 mg/L Cr(VI) solution was taken in each of six conical flasks and then known amounts of powdered *Millettia Ferruginea seed shell (MFSS*) were added in to each conical flask.

3.2. Apparatus and Instruments

The materials used in this study were shaker (KS-oscillator, Oven, China), electronic balance (Pw-254), suction filtration, pH meter (Jenway, UK), and Agilent Cary 60 Uv-visible spectrophotometer.

3.3. Chemicals and reagents

The chemicals used in this study were potassium dichromate, $K_2Cr_2O_7$ (Carelabmed, India) hydrochloric acid (HCl), 37% (Fluka Germany), sulphuric acid (H_2SO_4) 96% (Fluka Germany) sodium hydroxide (NaOH) assay > 97% (RPE, ACS-ISO for analysis), 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$ assay > 99% (Sigma Aldrich, India), and distilled water were used.

3.4. Preparation of stock solution.

A stock solution of Cr(VI) was prepared by taking a mass of 2.829 g of $K_2Cr_2O_7$ and dissolve in 1000 ml distilled water to get 1000 mg/L solution and 0.02 M H_2SO_4 was prepared by adding 1.1 ml of concentrated H_2SO_4 (96%) to 1000 ml distilled water. From the prepared 1000 mg/L Cr(VI)) concentration, high range standards (10, 20, 30, 40, 50, 60, 70, 80, 90, 100,) mg/L, and low range standards (0.1, 0.5, 1, 2, 3, 4 and 5) mg/L were prepared using serial dilution.

3.5. Preparation of adsorbents

Milletia *Ferruginea seed shell (MFSS)* was collected from near Addis Ababa University Arat Killo, and was washing several times to remove the impurities and dried at room temperature for several days. After drying the *Millettia Ferruginea seed shell (MFSS)* it was crushed into pieces to increase the surface area of the adsorbent. The crushed *powder* was repeatedly washed with distilled water until the colour of the adsorbent was completely removed, and was filtered by using succession filtration, finally dried in an oven at 80^0c for 85 minutes.

The prepared adsorbent is used for the present studies using adsorption process with the other parameters, pH, initial concentration, and time.

3.6. Instrumental methods

3.6.1. UV-Visible spectroscopy

The UV–Visible spectroscopy is the study of the absorption and emission of light and other radiation by matter, which analyses the absorption of ultraviolet light by chemical compounds at specific wavelength, and it gives qualitative and quantitative information. During the analysis process when the species absorb or emit electromagnetic radiation, atoms or molecules or ions moves from one energy states to another energy states.

For this study 0.02M H_2SO_4 was used before analysing the samples. In each low standard concentration 500 µg/L of 0.02M H_2SO4 and 500 µg/L of 1,5–diphenyl carbazide was added before the analysis of samples by UV- Spectrophotometer.

The analysis was carried out by using UV-Visible spectrophotometer. The analysis spectra of high range and low range concentration of Cr(VI) measurements were 340 nm and 540 nm wavelength respectively.

3.7. Adsorption study

3.7.1. Adsorption isotherms

For this study 10 ml of 30 mg/L Cr(VI) solution was taken in each conical flax's, covered with Para film and shacked at constant speed using Ks oscillator. The pH of the experimental solutions was adjusted to the desired pH (1, 2, 3, 4, 5 and 6) by the addition of 0.1 M HCl to the solution containing Cr(VI) ion and was measured by pH meter, until the pH value to be 1.

For the adsorption kinetics study 40 mg of powdered *Millettia Ferruginea seed shell (MFSS)* was added to the adsorbate solution with initial concentration of 30 mg/L in the time intervals (30, 60, 90, 120, 150, 180, 210, 240,) min.

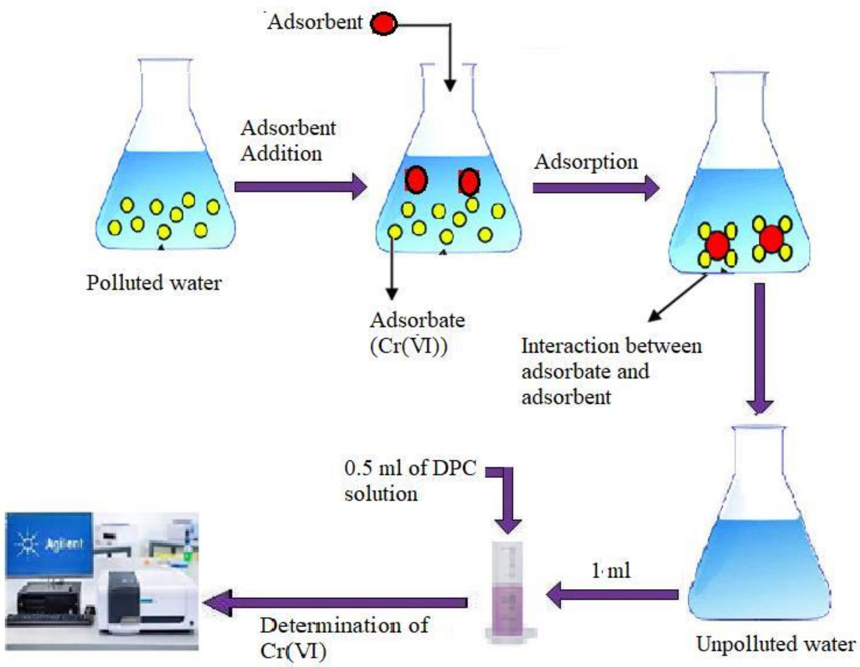

Figure1. Adsorption process for the removal of Cr(VI) from wastewater

The equilibrium adsorption capacity q_e (mg/g) and the percentage removal (%R) of Cr(VI) was calculated using equation 1 and 2.

$$q_e = \frac{1}{m}(Co - Ce)v \quad (1)$$

$$\%R = \frac{1}{Co}(Co - Ce)100 \quad (2)$$

Where q_e (mg/g) is the adsorption capacity of adsorbent for Cr(VI), C_o and C_e (mg/g) is the initial and equilibrium concentrations of Cr(VI) respectively, V (L) and m (g) are the volume and the mass of the adsorbent respectively [7].

Adsorption isotherm is an equation which relates the quantity of solid material getting deposited on to adsorbent surface and the equilibrium concentration of the solids in solution at known temperature.

$$\frac{Ce}{qe} = \frac{1}{KLqm} + \left(\frac{1}{qm}\right) C_e \qquad (3)$$

Where q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium and C_e (mg/L) is the equilibrium concentration of the adsorbate. q_m and K_L are maximum adsorption capacity (mg/g) and Langmuir constant respectively.

Langmuir and Freundlich are two parameter adsorption isotherm models used by several researchers. Langmuir isotherm model is the best model at which adsorption occurs at homogeneous sites and forms a monolayer on the adsorbent surface.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as:

$$R_L = \frac{1}{(1+KLC_o)} \qquad (4)$$

Where K_L is Langmuir constant and C_o is the highest initial Cr(VI) ion concentration (mg/L). The value of R_L provides information as whether the adsorption is irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1), or unfavourable (R_L>1).

$$q_e = q_m K_L C_e/(1+K_L C_e) \qquad (5)$$

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.

Freundlich isotherm model is an adsorption which occurs on the heterogeneous surfaces and forms multilayer adsorption.

Freundlich isotherm is a mathematical calculation for the adsorption equilibrium between a fluid (liquid or gas) and a solid substance.

Equation (6) and equation (7) represent non-linear and linear respectively.

$$q_e = K_F Ce^{1/n} \qquad (6)$$

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

$$\boldsymbol{ln\ qe = lnKF + \frac{1}{n} ln\ C_e} \qquad \textbf{(7)}$$

K_F (mg/g) (L/mg) is the Freundlich constant related to the multilayer adsorption efficiency and n is the heterogeneity factor represents the extent to which the adsorption depends on the equilibrium concentration. If $0 < \frac{1}{n} < 1$, desirable, if $\frac{1}{n} = 0$, irreversible, and $\frac{1}{n} > 1$ undesirable isotherm.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent.

3.7.2. Adsorption kinetic studies

Adsorption kinetics is a curve that describes the rate of release of a solute from an aqueous environment to solid face interface at a certain adsorbent dose and pH. The pseudo first order (PFO) and pseudo second order (PSO) models are widely used to describe the rate of adsorption in liquid solid interactions. The kinetic parameters, pseudo-first order and pseudo-second order models were tested to analyse the adsorption kinetics.

The kinetic model fits to pseudo second order (PSO) reaction plot by giving R^2 closer to 1 than the (PFO) kinetics. This indicates that the reaction is Chemisorption.

The pseudo-first-order equation is expressed as:

$$\mathbf{log}(\boldsymbol{q_{e-}\, q_t}) = \mathbf{log}\, \boldsymbol{q_{e-}}\ (\boldsymbol{K_1 t}) \qquad \textbf{(8)}$$

The pseudo-second- order equation is expressed as:

$$\boldsymbol{\frac{t}{q_t} = \frac{1}{K_{2\, q_{e}2}} + (\frac{1}{q_e}) t} \qquad \textbf{(9)}$$

Where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal at time t (min), k_1 the first-order reaction rate constant of adsorption ($mgg^{-1}min^{-1}$). The values of q_e and k_1 were calculated from the slope and intercept of the plot of ln(qe-qt) versus t, while the values of q_e and K_2 were evaluated from the slope and intercept of the plot of t/q_t versus t, respectively.

4. Results and Discussion

4.1. Analysis of chromium (VI) standard Calibration.

Figure.2 represents the UV-Visible spectra of different low range Cr(VI) concentrations in the range 0.1 mg/L to 5 mg/L. The absorbance versus wave length peak was observed at 540 nm wave length in the presence of 1,5-diphenyl carbazide complexing agent.

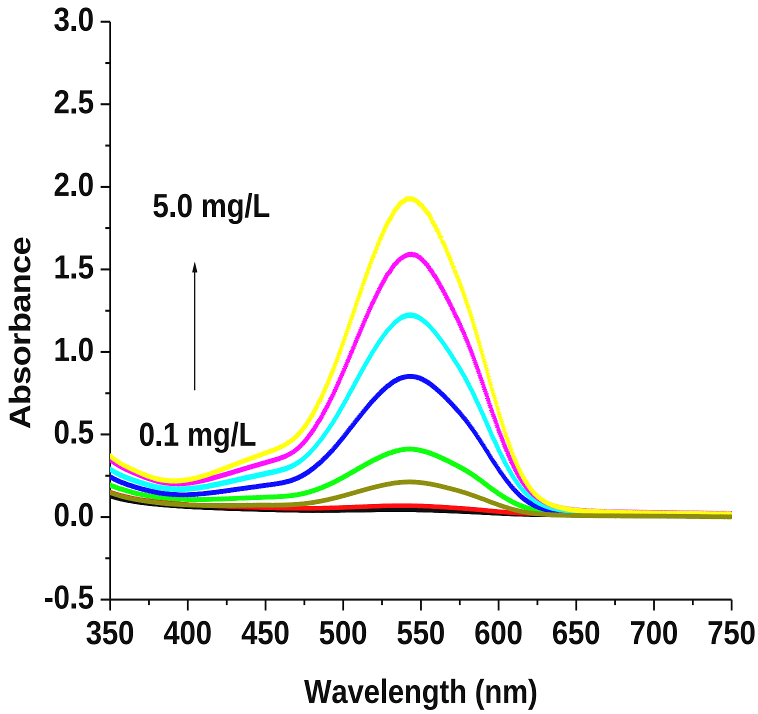

Figure 2.UV-Visible spectra of different low range Cr(VI) concentrations of 0.1 mg/L to 5 mg/L

Figure 3 shows UV-Visible spectra of different high range Cr(VI) concentrations of 10 mg/L to100 mg/L. The high range standard concentrations were measured using UV-Visible spectroscopy at 340 nm wave length without the complexing agent. The absorbance versus standard concentrations calibration curves and correlation coefficients of Cr(VI) were plotted as shown in Figure 4 and Figure 5, respectively. The correlation coefficient (R^2) of Cr(VI) for low range standard curve and high range standards were found to be 0.9996 and 0.9997, respectively.

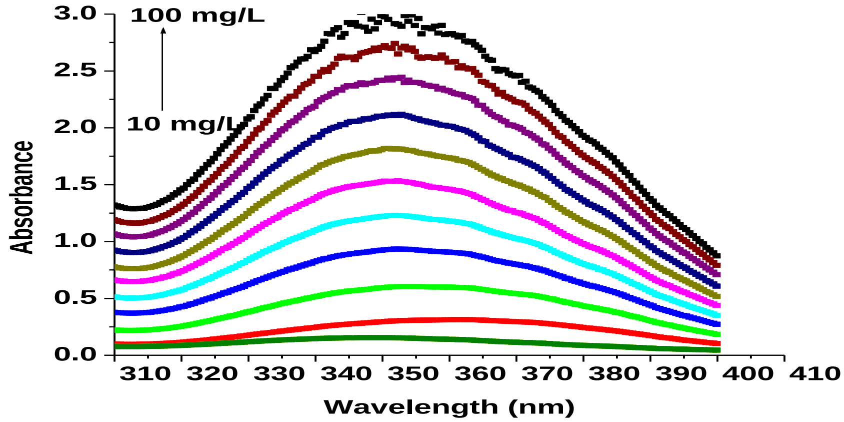

Figure 3. UV-Visible spectra of different high range Cr(VI) concentrations of 10 mg/L to 100 mg/L

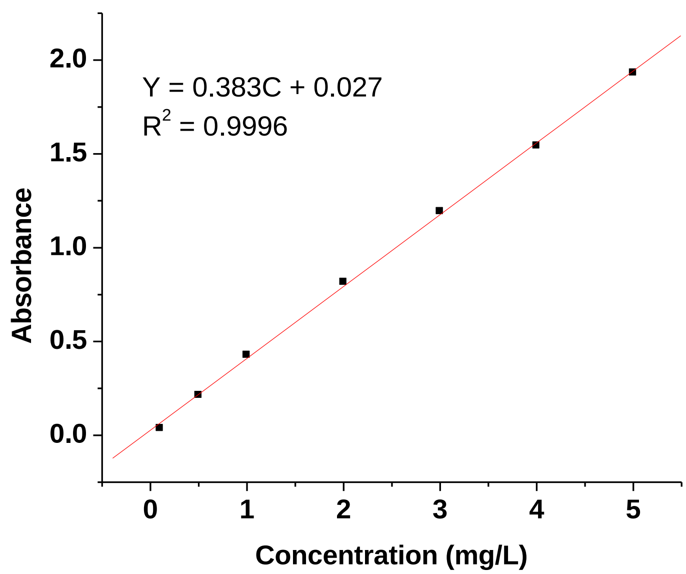

Figure 4. UV- Visible Standard Calibration curve of different low range Cr(VI) concentrations of 0.1 mg/L to 5 mg/L

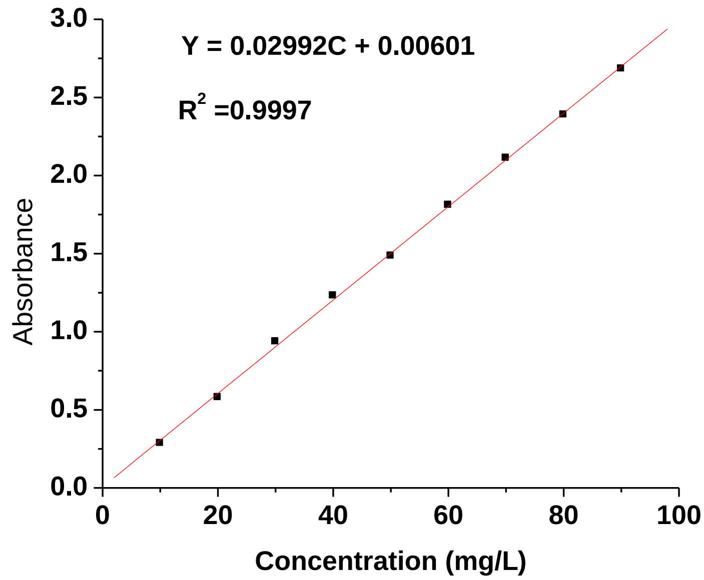

Figure 5. UV-Visible standard calibrations of different high range Cr(VI) concentrations of 10 mg/L to 100 mg/L

4.2. Optimization of Adsorption studies

4.2.1. Effect of pH

The influence of pH on the adsorption of Cr(VI) onto adsorbent was studied at different pH (1, 2, 3, 4, 5, and 6) as shown in Figure 6. The efficiency of elimination of Cr(VI) was highly influenced by pH. The highest adsorption was observed at pH=1, this can be attributed to the electrostatic attraction between the adsorbent and adsorbate. As the pH increase there is a decrease of hydrogen ion from the surface of the adsorbent, as a result an electrostatic repulsion force between the adsorbent surface and the incoming Cr(VI) ion, which leads to decrease the adsorption.

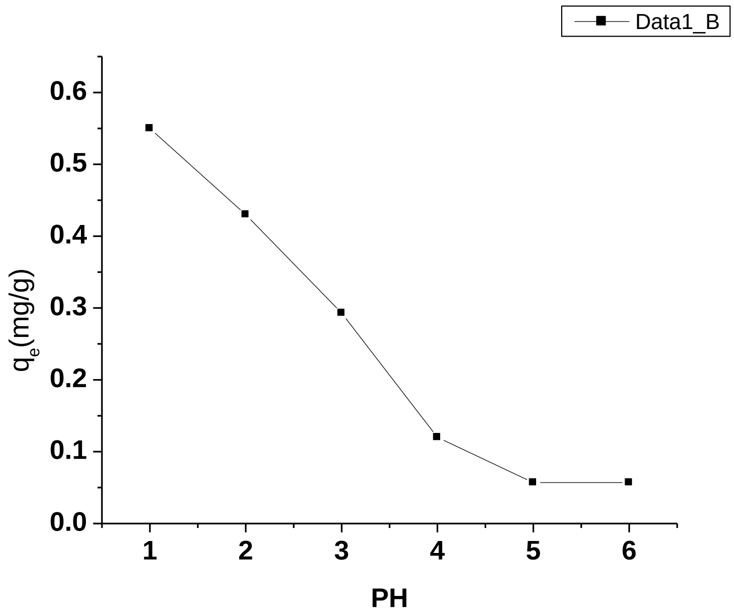

Figure 6.The effect of pH on the adsorption efficiency of Cr(VI) by *MFSS:* Conditions: adsorbent dose 30 mg, 10 ml volume and contact time 240 min.

4.2.2. Effect of contact time

The effect of contact time (30, 60, 90, 120, 150, 180, 210, 240 min) on the adsorption process were investigated and the results were shown in Figure 7.The adsorption capacity of Cr(VI) has sharply increased within the first 30 min and then steady increment was observed. This is because there are sufficient vacant adsorbent sites on the adsorbent surface while the slow increment is due to the saturation of the hexavalent chromium at the surface of the adsorbent.

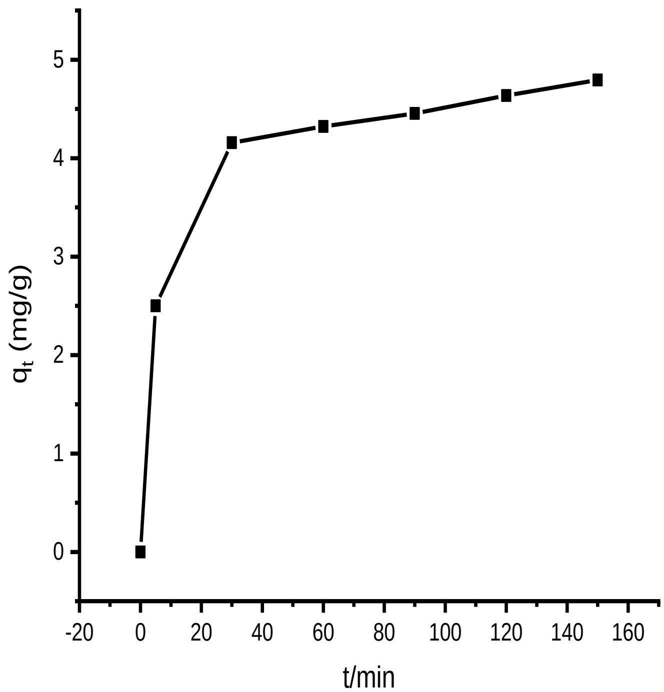

Figure 7**.** Capacity of adsorption of Cr(VI) on adsorbent MFSS. Conditions: at constant adsorbent dose (40 mg), volume 10 ml of 30 mg/L and pH 1.

4.2.3. Effect of adsorbent dosage.

The adsorption of Cr(VI) on to MFSS was studied by varying the adsorbent mass (10, 20, 30, 40, 50, and 60 mg) under optimized conditions as shown in Figure 8. Maximum adsorption was observed at 10 mg. The effect of adsorbent dosage on the removal percentage of Cr(VI) increases with an increase in adsorbent dose.

Maximum percentage removal was observed at 40 mg adsorbent dose while after maximum percentage removal there was a slight increase in Cr(VI) elimination. The percentage removal was 34.43% at 10 mg, 52.90% at 40 mg, and 55.97% at 60 mg. At equilibrium (beyond 40 mg) the percentage removal became nearly constant because of the saturation of the available active sites on the adsorbent.

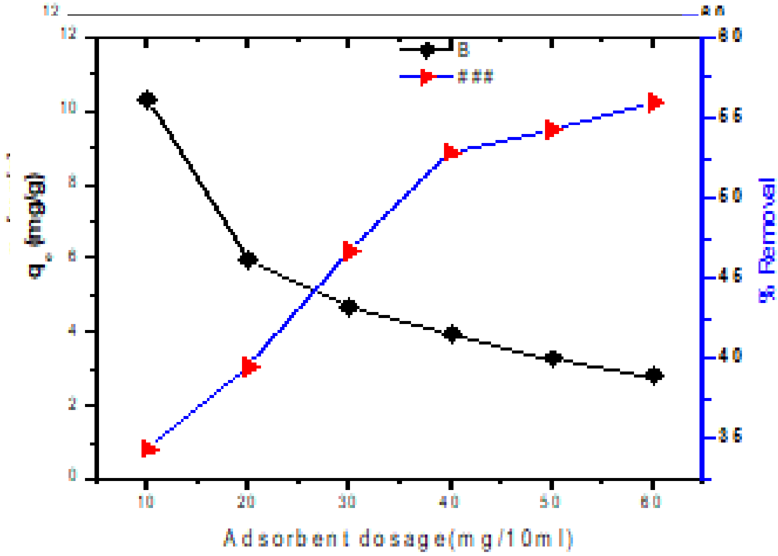

Figure 8. Plot of adsorption capacity and percentage removal of Cr(VI) versus adsorbent dosage of *MFSS:* Experimental conditions: volume10 ml of 30 mg/L, contact time 240 minute, and pH 1.

4.2.4. Influence of initial concentration

The effect of initial concentration of Cr(VI) on the adsorption process was conducted by varying the concentration from 10 mg/L to 100 mg/L for MFSS. Different concentrations of Cr(VI) (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100) mg/L were studied at pH 1, constant adsorbent dose 40 mg, contact time 240 min for MFSS. The adsorption capacities of Cr(VI) were increased with an increase in initial concentration of Cr(VI) and become constant. This is because at lower concentration there are sufficient active sites. However, at higher concentration active adsorbent sites are not sufficiently available for the incoming chromate ion to occupy. This is due to the electrostatic hindrance effect.

4.2.5. Adsorption isotherm models.

Figure 9 and Figure 10 shows Langmuir and Frundlich isotherm model of Cr(VI) adsorption on MFSS. The linear form of the two models was applied for calculation and the corresponding parameters are given in Table 4. The adsorption isotherm describes distribution of adsorbed substance between the solid and liquid when the adsorption reaches at equilibrium. The adsorption isotherm model of the experiment fits best with Freundlich isotherm model, indicating the adsorption takes place on to heterogeneous surfaces of the adsorbent. The adsorption capacity on the heterogeneous surface was 10.55 mg/g for *Millettia Ferruginea seed shell (MFSS).* The correlation coefficient of R^2 (0.983) is more inclined to the Freundlich isotherm model than the Langmuir isotherm model which is R^2 (0.953).

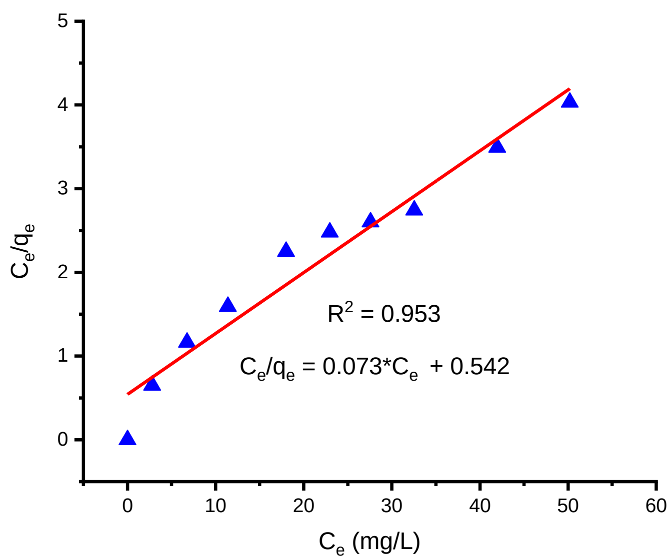

Figure 9. Langmuir model of Cr(VI) adsorption on MFSS, Experimental conditions: Adsorbent dose 40 mg, pH 1 and contact time 240 min.

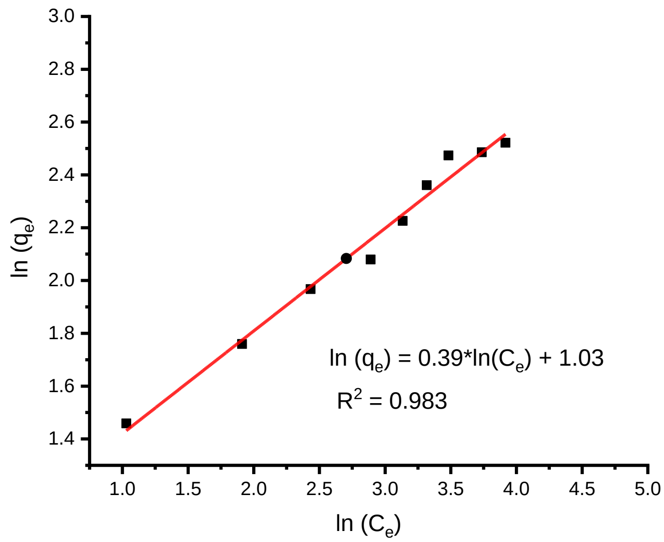

Figure 10. Freundlich isotherm model of Cr(VI) adsorption on MFSS, Experimental conditions: adsorbent dose 40 mg, and PH 1 and contact time 240 min.

Table 4. Langmuir and Freundlich isotherms for Cr(VI) adsorption on MFSS

Materials	Fitting models					
	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L(L/mg)	R^2	n	K_F	R^2
MFSS	13.70	0.135	0.953	2.564	2.801	0.983

4.2.6. Adsorption kinetic model

Figure 11 and Figure 12 represent pseudo-first order (PFO) and pseudo-second order (PSO) kinetic model of Cr(VI) adsorption on *MFSS*. The calculated parameters, Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are illustrated in Table 5. The higher correlation coefficient (R^2) values (0.999) obtained from the pseudo-second-order (PSO) kinetic model compared to the correlation coefficient (R^2) of the pseudo-first-order (PFO) kinetic model (0.916) is closer to pseudo-second-order kinetic model for *MFSS* adsorbent. This indicated the adsorption takes place on to the heterogeneous surfaces of the adsorbent.

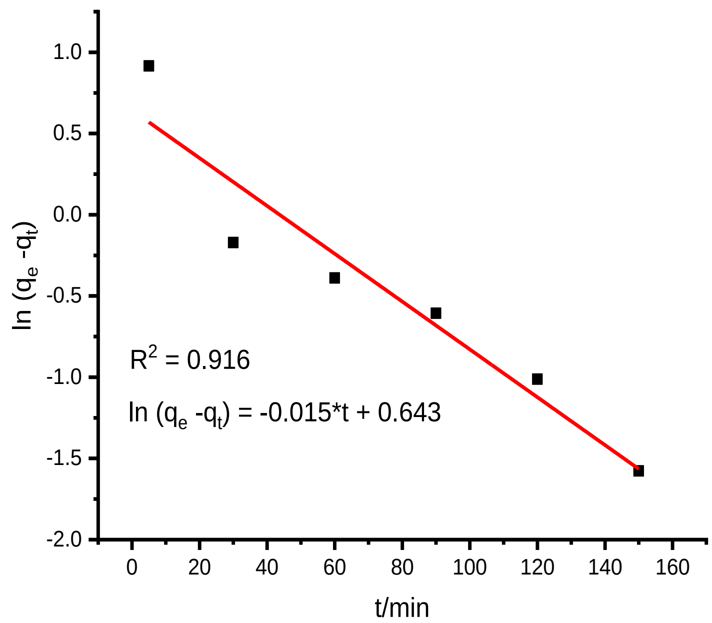

Figure 11. Kinetic plot (pseudo first order) for the removal of Cr(VI) on adsorbent MFSS, experimental conditions: adsorbent dose 40 mg, pH 1, and volume 10 ml.

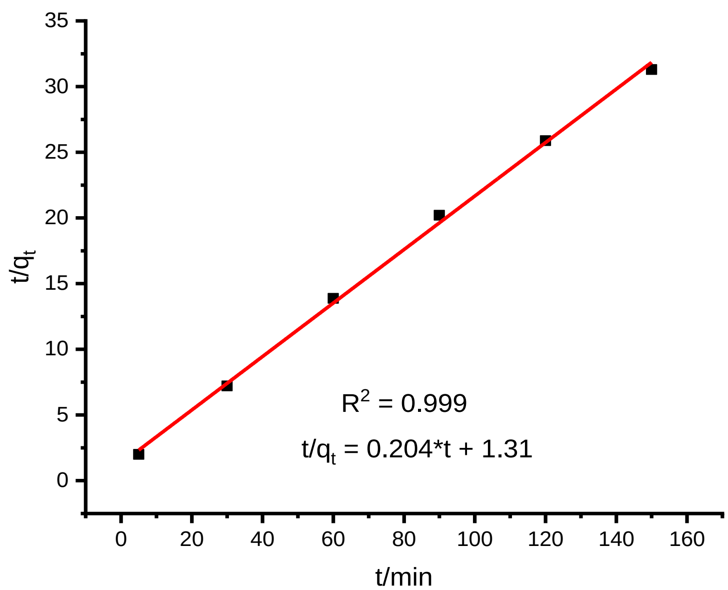

Figure 12. Kinetic plot (pseudo second order) for the removal of Cr(VI) Using MFSS adsorbent. Experimental conditions: adsorbent dose 40 mg, volume 10 ml, pH 1.

Table 5. Kinetic parameters of pseudo-first order and pseudo-second order equations for Cr(VI) on adsorbent MFSS.

Kinetic model for MFSS						Experimental data, q_e (mg/g)
Pseudo-first order			Pseudo-second order			
K_1 (min^{-1})	q_{cal} (mg/g)	R^2	K_2 (g/mg/(min)	q_{cal} (mg/g)	R^2	
0.015	1.90	0.916	0.032	4.90	0.999	5.00

4.2.7. Comparison of the adsorption capacity of the adsorbent with literature reports

Locally available unmodified adsorbents were selected for comparison from different literature. The adsorption capacity of MFSS compared with other adsorbents for Cr(VI) ion taken from different literature are given in Table 6 for comparison. The maximum adsorption capacity of Cr(VI) under this study was better than the other selected literature adsorbents. The adsorption capacity of the selected adsorbents varies between 6.81 and 10.55.

Table 6. Comparison of adsorption capacity of different adsorbents

Adsorbents	Adsorption capacity (mg/g)	References
Cranberry kernel shell	6.81	2
Banana peel	10.2	2
Papaya peels	7.16	17
Avokado kernel shell	10.08	17
Banana peels	10.42	17
MFSS	10.55	Present work

5. Conclusion

Adsorbent MFSS has demonstrated an effective adsorbent for Cr(VI) adsorption whose adsorption capacity is 10.55 mg/g. In addition, maximum removal percentage was found to be 55.97% which suggests strong adsorption ability. When examining the kinetic models, the correlation coefficient (R^2) for the pseudo-second-order model was found to be 0.999. This is significantly closer to 1 compared to the pseudo-first-order model's R^2 of 0.916, further indicating that the process is primarily chemisorption. Also, the adsorption equilibrium aligns with the Freundlich isotherm, suggesting that adsorption occurs on a miscellaneous face of MFSS. Comparison of adsorption capacities of low cost and locally available adsorbents from literature with the present studies, the adsorption capacity of MFSS is better. If this adsorbent material is carbonized the efficiency of the adsorption capacity is expected more than the obtained value.

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