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Removal of Heavy Metals from Wastewater Using Albizia Lebbeck Seed-Based Activated Carbon

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ABSTRACT

Water, a vital resource for sustaining life, is increasingly threatened by pollution caused by industrialization, population growth, and modernization. This study evaluates the potential of Albizia lebbeck seed-based activated carbon for the removal of Chromium VI [Cr (VI)] ions from aqueous solutions. The Albizia lebbeck seed was chemically modified using phosphoric acid into activated carbon and its performance was tested based on contact time, adsorbent dosage, temperature, concentration, and pH of the wastewater. The efficiency of the preparation was evaluated using batch adsorption isotherm, Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and Energy Dispersive X-ray Spectroscopy (EDS). Batch adsorption results revealed that the removal of Cr (VI) ions from its aqueous solution on the studied adsorbents was influenced by the investigated parameters in varying degrees. The adsorption process was found to be endothermic and best described by the Freundlich as determined from isotherm modelling. The FTIR analysis also show the presence of more surface functional groups and sharper peaks in the activated adsorbent than the original form. The SEM microgram revealed the morphology of the prepared activated adsorbent and the activated adsorbent exhibited higher BET surface area (336.436 m2/g), pore volume (0.305 cc/g), and pore size (6.602 nm), enhancing its mesoporous nature compared to the unmodified adsorbent (236.617 m^2/g), (0.215 cc/g) and (6.214 nm) which likely improved its performance. The results confirm that activated Albizia lebbeck seeds are effective adsorbents for removing chromium (VI) ions from aqueous solutions, particularly when treated with inorganic acid. This highlights their potential for removing heavy metal contaminants from industrial wastewater.

Keywords: *Activated Carbon, Albizia Lebbeck Seed, Wastewater, Heavy Metals*

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1. INTRODUCTION

The rapid industrialization and urbanization of modern society have led to a significant increase in the generation of wastewater contaminants with heavy metals [1]. Heavy metals such as lead Pb), Cadmium (Cd), and Nickel (Ni) are highly toxic and can cause severe environmental and health problems, even at low concentrations. The removal of heavy metals from wastewater is therefore a critical environmental concern. Water is the most important and essential resource on Earth for maintaining life's basic processes, but regrettably, economic expansion, population growth, modernization, and other physical and biological changes are all causing its quality to continue declining, which has a negative effect on both human health and the environment as a whole [2-3]. Advancements in human procedures since the days of the Industrial Revolution have charted the course of industrial processes towards utilizing the full potential of water, especially as a process utility. Unfortunately, this has also rendered water bodies vulnerable to untreated or partially treated wastewater that are end products of industrial processes. These wastewaters are laden with heavy metals like Chromium which when taken up by living things in water bodies even at very low concentrations, can result into irremediable consequences in them [6-7]. The bioaccumulation tendencies of heavy metals enable them to be transferred to the apex of the food and this makes them highly risky to ingest. In addition to industrial and consumer waste, acid rain can also release heavy metals into streams, lakes, rivers, and groundwater [8]. Due to the rapid expansion of sectors, heavy metal wastewater is rapidly being discharged into the environment, particularly in developing nations, through facilities such as metal plating, mining, fertilizer production, textile making, battery production, paper production, and pesticides [9].

As such, the world continues to struggle with the environmental challenge of effective waste disposal even as it urgently seeks to surpass previous advancements and meet endless human needs on an industrial scale. As a result, special legal and social attention is placed on industries on a global scale to ensure that the possible disaster that may result from large concentrations of heavy metals in water bodies is averted [10-11]. In many developed countries, stringent penalties are meted out to industries that release these heavy metals into water bodies, ensuring that pollution of the water bodies is kept to the minimum. Unfortunately, similar policies and measures are not widely implemented in most developing countries, leaving the poor people who depend solely on water from polluted water bodies vulnerable to diseases and infection that result from the deposit and synthesis of heavy metals into living organisms [12]. Hence, researchers need to elaborate on economically sustainable means of solving wastewater problems to carry developing nations along as they rapidly industrialize to bridge the gap with developed countries [13-14].

Many methods have been explored for the removal of heavy metals from wastewater but adsorption in particular stands out as the most economical and effective method in removing a wide variety of harmful heavy metal substances from industrial wastewater [15]. Several materials have been evaluated as suitable adsorbents such as biomass because they are good sources of carbon: animal wastes, fruit wastes (fruit peels and seeds), aquatic plants, wood-based materials (sawdust, wood shavings, the bark of trees) and agricultural wastes. The availability, cost of acquisition, porosity and presence of certain functional groups on the biomass surfaces make them excellent materials for adsorption processes [16-17]. In addition, the surface area, chemical stability and regenerability of carbon-based substances are major factors that ensure adsorption occurs on their surfaces thereby making them favourable as choices of adsorbents [18].

Several studies have been conducted on the potential of Albizia Lebbeck as an adsorbent for purifying industrial wastewater. Activated biochar obtained from the pods, leaves and seeds of the Albizia lebbeck plants have shown potential in adsorption, especially in removing heavy metals from industrial wastewater [19]. The plant is grown widely and exists both through natural propagation and through plantations by humans. Its ability to thrive in various climatic conditions makes it a favourable choice as a source of adsorbent. The relative availability of the trees makes it an excellent source of adsorbent material however, most previous studies have been focused on adsorbents derived from the pods of the plant thus there is a need to evaluate the potential of other parts of the plant such as the seeds and leaves [20].

Thus, this research aimed at synthesizing, characterizing, and applying Albizia lebbeck seeds-derived adsorbent for the removal of chromium VI ions from its aqueous solution; Sourcing and preparation of seeds obtained from Albizia lebbeck trees, carbonization, and activation of the seeds, characterization of both activated and raw adsorbents using BET, FTIR and SEM-EDS techniques, application of the activated adsorbent in adsorption experiment for the removal of chromium (VI) ions from simulated solution and determination of best adsorption isotherm model for the description of the adsorption process. This study was limited to the preparation, characterization, and activation of Albizia lebbeck seeds-derived adsorbent and testing its effectiveness in removing chromium from its aqueous solution.

2. EXPERIMENTS

The activated carbon was prepared from Albizia Lebbeck seed through chemical activation with phosphoric acid. Stock solution of Pb(II), Cd(II) and Ni(II) were prepared using their respective nitrate salts. Wastewater samples were collected from local industrial effluent treatment plant and all these reagents used were of analytical grade.

2.1 Sample Collection and Preparation of the seeds

Albizia lebbeck pods were collected from the University of Ilorin premises. The seeds were thoroughly washed with tap water, followed by distilled water. They were then purified by soaking in a 0.1 M HCl solution for 24 hours, rinsed with deionized water until a neutral pH was achieved, air-dried at room temperature for three days, and stored in glassware for further analysis.

2.2 Preparation of Un-modified Albizia Lebbeck seed adsorbent

The dried seeds were placed in the muffle furnace for 2 hours 30 minutes at 300°C. The biochar obtained was then crushed to powder using mortar and pestle and sieved with a 53 µm sieve respectively. The sieved powder was washed repeatedly with deionised water until a colourless filtrate was obtained to remove any traces of absorbed salt. Subsequently, the residue was dried in an oven at 105°C for 10h after which it was cooled, stored, and labelled in a sterile sample container as un-modified Albizia lebbeck seed (ALS).

2.3 Preparation of Modified Albizia Lebbeck seed adsorbent

Some parts of ALS were carbonized for 2:30 h in a muffle furnace at 300°C before chemical activation with 1 M Phosphoric acid (H_3PO_4) for 72 hours. After activation, the sample was washed with deionised water to remove any unreacted material and oven dried at 105°C after which it was stored as Chemically activated Albizia Lebbeck Seed (CMALS).

2.4 Catalyst Characterization

Fourier Transform Infrared (FT-IR) spectroscopy was used to analyse the functional groups on the adsorbents while the surface area, pore volume, pore diameter, and pore size distribution were determined using Brunauer-Ennett-Teller (BET) analysis. The surface structures and compositions were determined by Scanning Electron Microscope (SEM) coupled with energy-dispersive X-ray Spectroscopy (EDS) Analysis.

Proximate analysis is a laboratory technique used to determine the approximate composition of material, typically biomass or coal. The analysis has to do with the determination of the material's ash content, moisture content, volatile matter and carbon content.

For moisture content, a pre-weighed crucible was filled with 1 g of the adsorbent, which was then sealed with a covering. The sample's complete mass, including the container itself and cover, was measured. After being loaded with samples, the container was placed in an oven without its cover. The oven was heated to 110°C for three hours to ensure that the sample weights were consistent. The process was repeated three times, and the moisture percentage was determined using equation 1 [22].

$$\text{Moisture content (\%)} = \frac{(B-F)}{(B-G)} \times 100 \qquad (1)$$

B is the mass of container with lid + original sampling.
F is mass of container with lid + dried sampling
G is the mass of container with a lid.

To check for the ash content in the sample, an open crucible was filled with 5g of the material, and the resulting mass was measured. The sample was heated to 900°C for 3 hours. The material was measured after being cooled to room temperature. The process was repeated three times. The ash content was determined using equation 2:

$$\text{Ash content (\%)} = \frac{(A-C)}{(K-C)} \times 100 \qquad (2)$$

C is the mass of empty crucible in g
K is the mass of crucible + original sample
A is the mass of crucible + ash sample in gram

2.5 Adsorption Experiments

Batch experiments were conducted to determine the adsorption isotherms of synthetic wastewater onto the adsorbents in a glass flask. The experiments were conducted at room temperature to be indicative of climatic conditions and the impacts of interaction duration, temperature, as well as adsorbent dosage on the decline in heavy metal concentration were examined [23]. A certain volume of the synthetic wastewater sample was measured into series of graduated flasks. The kinetics of the adsorption was studied at different time intervals (5-90minutes) using a certain mass of adsorbent added into solutions in the flasks. The effect of temperature was investigated at different temperatures. The effect of pH was also studied within the range of 2 – 12 by making adjustments where necessary with NaOH or HCl. The mixtures were filtered, and the residual concentrations of the heavy metal were determined.

2.5.1 Effect of Contact Time

Contact time refers to the duration for which the contaminated water is in contact with activated carbon. Initially the rate of adsorption is rapid as the available active sites on the carbon surface are occupied by heavy metal ions. As time progresses, the rate of adsorption decreases and eventually reaches an equilibrium point where no significant changes in metal concentration occur. Determining the optimal contact time is crucial for maximizing the removal efficiency. Studies have shown that the longer contact times generally leads to higher removal rates, but at some point, the increase in removal efficiency diminishes. At 120 minutes equilibrium is attained. Therefore, it is essential to identify the equilibrium time to optimize the process and reduce costs.

2.5.2 Effect of pH

The pH of solution significantly influences the adsorption capacity of activated carbon for heavy metals. Different metals exhibit varying solubility and ionization states at different pH levels. For instance, at low pH, the concentration of H^+ ions is high, which can compete with metals for ions adsorption sites on activated carbon, potentially reducing removal efficiency. The method of adsorption was performed at multiple pH levels (2, 4, 6, 7, 8, 10 and 12) for the starting concentration, constant adsorbent dosage, and constant contact time were observed in order to investigate the impact of the pH on the adsorption of heavy metals from synthetic wastewater. The Optimal pH range was neutral to slightly alkaline pH (around 6 – 8) is favourable for the adsorption of many of the heavy metals. However, the pH can vary depending on the specific heavy metals being targeted.

2.5.3 Effect of Temperature

Temperature plays a dual role in the adsorption process. An increase in temperature can enhance the kinetic energy of the molecules leading to increased diffusion rate and potentially higher adsorption capacities. However high temperatures may also disrupt the adsorption process by desorbing metal ions from the activated carbon surface. The optimal temperature for heavy metal removal using Albezia lebbeck seed-based activated carbon falls within the range of ambient to moderately elevated temperatures (20 – 50 ^{o}C). beyond this range, the benefit of increased kinetic energy may be outweighed by the desorption effect.

2.5.4 Effect of Concentration

The initial concentration of heavy metals in the solution directly impacts the adsorption capacity of activated carbon. Higher concentrations of metal ions can lead to increased driving force for adsorption, resulting in higher removal efficiencies. However, once the active sits on the carbon are saturated, the removal efficiency will be low. Optimal concentration is essential to determine the saturation point of the activated carbon. The six concentrations were; 120 ppm, 80 ppm, 60 ppm, 50ppm, 40 ppm and 20 ppm. It was observed that the percentage removal of chromium increased with the potassium dichromate solution

2.6 Adsorption Kinetics

Adsorption Kinetics is a process by which solute molecules attach to the surface of an adsorbent. Adsorption kinetics is a line or curve that explains the rate of retention or release of a solute from an aqueous to solid-phase boundary at a specified adsorbent dose, temperature, flow rate and pH.

2.6.1 Pseudo-First Order Kinetics Model

Pseudo first order kinetics model describes solute adsorption unto adsorbent following the first order mechanism, the following formulars represents the pseudo first order reaction kinetics

$$\frac{de}{dt} = k1\ (qe - qt) \qquad (3)$$

This equation could further be expressed as

$$Log\ (qe - qt) = log\ log\ qe\ - \frac{k1}{2.303xt} \qquad (4)$$

Where;

$qe = amount\ of\ adsorbate\ at\ equiliruim$ (mg/g)
$qt = amount\ of\ adsorbate\ adsorbed\ at\ time\ t$ (mg/g)
$k1 = rate\ constant\ of\ pseudo\ first\ order\ per\ minutes$ (min^{-1})

2.6.2 Pseudo – Second Order Adsorption

According to the pseudo-second order kinetics model, the concentration of metallic ions inside any fluid in question and the number of open adsorption sites on the adsorbent's outermost layer are both important factors in the adsorption process. The sole disparity between the pseudo-second-order kinetic model and the pseudo-first-order kinetic model is the speed of the model. This is proven by the pseudo-second order kinetics rate equation may be express equation 5 and 6.

$$\frac{de}{dt} = k1\ (qe - q)^2 \qquad (5)$$

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{k2qe} + \frac{t}{qe} \qquad (6)$$

Where $k2 = the\ rate\ constant$ pseudo- second order sorption (mg/min)

2.6.3 Elovich Kinetics model

According to the Elovich equation, neither desorption nor the interactions among the species that are absorbed could substantially alter the rates of adsorption at minimal coverage because the solid surface is assumed to be inherently heterogeneous. The Elovich kinetics model suggests that the adsorption of the heavy metal ions onto the activated carbon is a complex process involving multiple mechanisms, such as surface adsorption and pore diffusion. The model parameters (α and β) provides valuable insights into the adsorption kinetics and capacity.The following represents the Elovich dynamics model mathematically as:

$$\frac{dq}{dt} = \frac{1}{\beta in(\alpha\beta)} - \frac{1}{\beta in(t)} \qquad (7)$$

where:

$\frac{dq}{dt}$ is the rate of adsorption
α is the initial sorption rate (mgg^{-1}min^{-1})
β is the desorption constant (g.mg^{-1}).
q is the amount of adsorbate adsorbed at time t.

2.7 Adsorption Thermodynamics

Thermodynamic factors are crucial for determining whether the adsorption process is feasible and spontaneous. The thermodynamics parameters generally give an understanding into the minimum kinetic energy required for the adsorbate to become bound to the adsorption site. Usually, the nature of the adsorption process which are the main factors that control viability and spontaneity are thermodynamic parameters, specifically heat of enthalpy (H), Gibbs free energy (G), and entropy (S). The Langmuir isothermal constant ($C_{ad,e}$), the solvent coefficient distribution (K_d), and the equilibrium content (C_e), which varies with temperature, are all provided in the equations below were used to determine the thermodynamic parameters in this research.

$$In\ K_d = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

For the Langmuir constant

$$InK_c = \frac{C_{ad,e}}{C_e} \tag{10}$$

$$\Delta G = -RTInK_c \tag{11}$$

ΔS can also be obtained by Gibbs- Helmholtz equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{12}$$

3. RESULTS AND DISCUSSION

3.1 Characterization

The Modified Albizia lebbeck seeds (MALS) and the unmodified calcined Albizia lebbeck (ALS) were analyzed for their surface area, pore volume and pore size of all the absorbent were analyzed using BET under N_2 adsorption-desorption study and the results are presented in Table 1. The results showed that the modified adsorbent has higher surface area which serves as an indicator that they may have higher adsorption capacity. It was also observed that the modified Albizia lebbeck seed (MALS) adsorbent has a higher surface area compared to the unmodified [24].

Table 1. BET Analysis of Modified and Unmodified Adsorbents.

Sample	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Size (nm)
ALS	236.617	0.215	6.214
MALS	336.436	0.305	6.602

The enhanced surface area of MALS may be attributed to incorporation of the phosphoric acid as a synthesizing agent, which may have improved the MALS because the pore size of this adsorbent was about 6.602 nm which indicated that they are more mesoporous in nature compared with the unmodified adsorbent (ALS) with pore size 6.214 nm. It follows that adding acid to the adsorbent during synthesis can change its surface characteristics, resulting in an increase in porosity and surface area. It is expected that due to such desirable properties adsorption capacity and reactivity is enhanced, making it more effective for capturing ions from a solution [1]. BET test is significant because it provides valuable insights into the surface properties and porosity of materials, which are critical for understanding their behaviour in various applications.

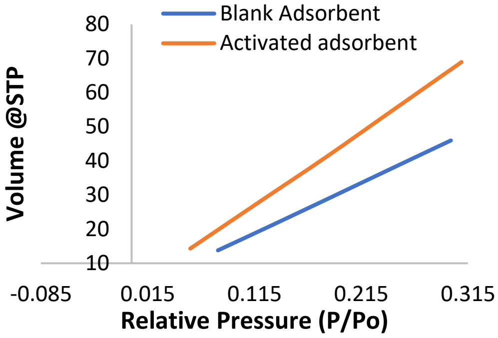

Figure 1. Relative Pressure vs Volume at STP for Blank and Activated Adsorbents.

The SEM analysis shows the nature of the Albizia lebbeck seeds activated adsorbent, and it elaborates on the clarity of the development of pores which are pivotal to adsorb the chromium heavy metal unto the Albizia lebbeck seed adsorbent. The SEM figure below show the analysis images for the modified Albizia lebbeck seed adsorbent after synthesis with phosphoric acid, by Scanning Electron Microscopy (SEM). The images show the SEM analysis at 500, 1000 and 1500 magnification. The images depict how the particles in the adsorbent are in aggregated form instead of in separated forms, which can be attributed to the large surface area of the adsorbent. The SEM images show a highly irregular and rough appearance on the surface which may be due to synthesis with the auto phosphoric acid (Figure 2A). The irregular and rough appearance when observed after SEM analysis is valid indicator of a good adsorbent [25-26].

Pores were evident on the surface of the modified Albizia lebbeck seeds (MALS) after the SEM analysis, which can be attributed to the presence of an elementary pore network [24][27]. The evident elementary pores can be most observed on the Figure 3a below which is a 1500X view of the surface of the adsorbent. The Figure 2B best depicts the extent of the coarseness and roughness of the adsorbent with SEM analysis. Figure 2C draws into perspective the active pores in addition to the roughness of the adsorbent.

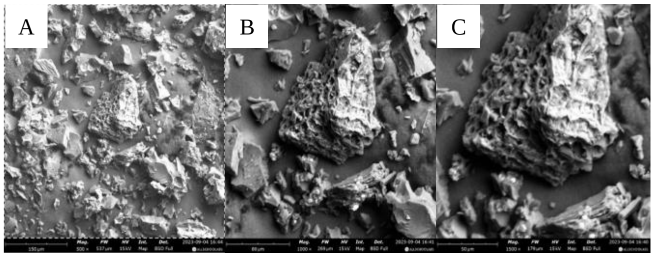

Figure 2. Micrographs of Modified *Albizia lebbeck* Seed Adsorbent at (A)500x, (B) 1000x, and (C) 1500x magnification

The Energy Dispersive X-ray Spectroscopy (EDS) Analysis technique used to determine the elemental composition of the modified albizia lebbeck seeds sample. The peaks observed in the spectrum show the composition of the elements present in the MALS adsorbent. It can be seen from the spectrum plotted below that C, O and Si are present on the surface of the MALS adsorbent. As it can be observed from the Figure 4a, the carbon composition in the adsorbent is far greater than for the rest of the other elemental compositions. From background studies on adsorption, the higher the carbon content the more desirable the adsorbent is. The large amount of carbon is synonymous with the high carbon composition that can be seen from literature studies [28].

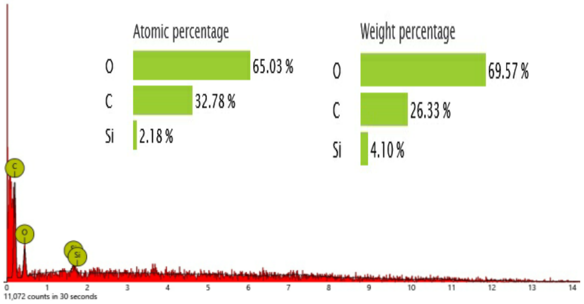

Figure 3. EDX Spectra, atomic percentage and weight percentage of Modified *Albizia lebbeck* Seed Adsorbent

Accuracy of EDS can be affected by a variety of factors. These factors might affect the chemical composition or nature of the albizia lebbeck seeds adsorbent. One of the major factors that might show inconsistency is the fact that the analysis is focused on a particular section of the adsorbent, which might not pick up elemental compositions present only in other parts of the adsorbent. The presence of negligible silicon (as shown in Figure 3) on the adsorbent surface maybe attributed to partial contamination during the course of preparation of the adsorbent. Silicon is generally chemically stable and inert, which means it is less likely to react with adsorbates.

The FTIR technique is a pivotal means in order to unravel the intricacies of functional groups present in the adsorbent and to predict the interaction with the adsorbate as a result of the functional groups present [29]. These groups are specific arrangements of atoms within the adsorbent's structure that can interact with adsorbate molecules, influencing adsorption capacity, selectivity, and other adsorption-related properties. The spectra were collected in the range from 400 cm^{-1} to 4000 cm^{-1} (Figure 4). It was observed that the while that unmodified spectrum has about 10 peaks, the modified adsorbent (MALS) possessed more than 20 peaks within its spectrum. The presence of more peaks in the modified adsorbent’s spectrum can be said to be function of the synthesis of the MALS with an acidic agent. A higher number of peaks in the FTIR spectrum of the modified adsorbent suggests greater chemical complexity and diversity within the sample. Diversity and complexity depicted in the spectrum of the modified adsorbent reflect heavily on the expected broader selectivity affinity of the modified adsorbent to target contaminants [30].

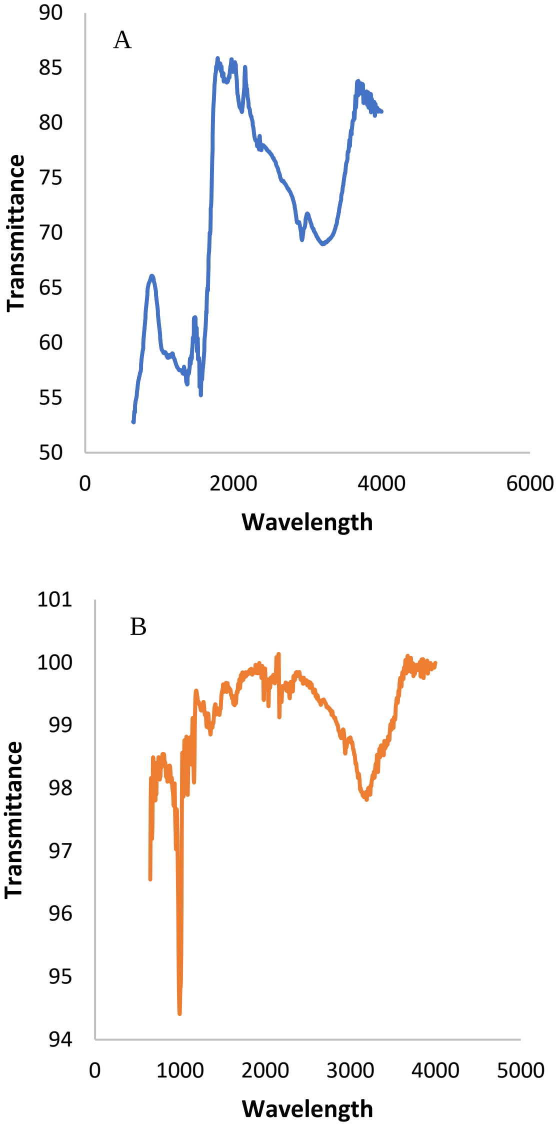

Figure 4. FTIR Spectra of (A) Blank and (B) Modified *Albizia lebbeck* Seed Adsorbents

The important peaks represented are the C-H bond which is stretching vibration, indicating the presence of alkyl groups, the O-H bond which indicates the presence of hydroxyl groups, the C=C bond and C-O bonds indicates the presence of carbon and carboxyl groups [7]. The Figure 4A and the Figure 5B show the plots of the activated and blank adsorbent. The high range of values for transmittance on the FTIR plot for the activated adsorbent can be attributed to several factors related to the changes in the adsorbent's structure, composition, and surface properties during the activation process. The activation process generated more active sites with functional groups. This increased availability of functional groups contributed to higher transmittance values due to enhanced adsorption [31].

It is clear that for the unmodified Albizia seed adsorbent the absorption peaks observed at about 3201cm^{-1} indicate the presence of the O-H group due to alcohol or phenol [32]. The peaks observed at about 1118cm^{-1}

indicates the presence of C-O bond within the unmodified Albizia seed adsorbent. The peak observed at the range of 13700 to 1400 for the unmodified adsorbent indicates the presence of C-H bond within the adsorbent. The peak number between $3000cm^{-1}$ and 3980 indicate a high density of various functional groups in the fingerprint section of the spectra. The peaks observed between $3200cm^{-1}$ and 3260 cm^{-1} indicate the presence of the O-H bond in the modified adsorbent. The observable peaks seen between $2850cm^{-1}$ and $2960cm^{-1}$ indicated the presence of C-H functional group in the adsorbent compound. The observable peaks between $1650cm^{-1}$ and $1800cm^{-1}$ indicate the presence of C=O functional group in the adsorbent between $1400cm^{-1}$ and $1600cm^{-1}$, the observable peaks detected signify the presence of C-C bond within the adsorbent spectra. Observable peaks around $2300cm^{-1}$ were attributed to the presence of C≡C bonds in that range of the spectra. Peaks observed between $1100cm^{-1}$ and $1300cm^{-1}$ could also serve as an indication of the presence of phosphates (P=O) as a result of synthesis of the adsorbent with autophosphoric acid. The greater number of peaks seen in the modified Albizia seed adsorbent as compared to the unmodified Albizia seed adsorbent elaborates on the effect of the synthesizing agent that has been added to the Albizia lebbeck seed adsorbent to increase its adsorption efficiency. Hence, the modified adsorbent contains more functional groups than the unmodified adsorbent ensuring greater adsorption efficiency during the experiment.

3.2 Physiochemical Study of Albizia lebbeck Seeds Adsorbent Biomass

The physiochemical study of Albizia Lebbek seed adsorbent biomass reveals its potential as low-cost, eco-friendly adsorbent for removing various pollutant from waste water. After a preliminary carbonization process to check for the optimum duration and temperature for carbonization, the ideal carbonization conditions were set at 300°C and 2.5 hours instead of the initial 400°C for 1.5 h.

Table 2. The summary of the carbonization process

Temperature	300 °C
Time	2.5 hours
Initial weight (g)	112.32
Final weight (g)	46.13

The Bulk density is a measure of the mass of the Albizia lebbeck seeds adsorbent per unit volume. The Bulk density measures how tightly the adsorbent particles are packed together. Adsorbents with higher bulk densities generally have more tightly packed particles. Proper packing ensures uniform flow distribution of the fluid (gas or liquid) through the adsorbent bed, reducing channelling and improving the adsorption efficiency. As it can be seen, the bulk density of the Albizia seed adsorbent is 0.865 meaning the biomass has undergone carbonization at high temperature and it can be deduced that it has high packing quantity of solid and can hold much adsorbate [33].

The Ash content in the Albizia seed adsorbent refers to the non-combustible residue left behind after the adsorbent material has been subjected to high temperatures. This residue typically consists of minerals, inorganic impurities, and other non-volatile substances. Impurities in the ash may interfere with the adsorption process by occupying active sites on the adsorbent surface, reducing the available surface area for adsorption, and affecting the selectivity of the adsorbent. An ash content of about 0.97% as shown in Table 3 is satisfactory as it shows that there is a very low amount of ash and possible impurity accompanied with it [34].

Moisture content can affect the adsorption capacity of the Albizia seeds adsorbent. When an adsorbent contains moisture, some of its surface area and pore space may be occupied by water molecules. This can reduce the available sites for adsorption of the target substances. In some cases, moisture itself can be the target of adsorption. A moisture content of about 6% as shown in Table 3 is fairly satisfactory. As opposed to Moisture Content, the Percentage Dryness of about 94% as shown in Table 3 is a strong indicator that the adsorbent is fairly satisfactory for storage and adsorption process.

Table 3. The physiochemical analysis of the Albizia lebbeck seeds derived adsorbent

Parameters	Value
Bulk density	0.86
Ash content (%)	0.97
Moisture content (%)	6.00
Dryness content (%)	93.9

3.3 Batch Experiment Studies

The batch adsorption studies were undergone with five predominant factors in consideration: pH, time, adsorbent dosage, temperature and initial concentration. Figure 5 below depicts the calibration curve which is a graphical representation of the relationship between absorbance and concentration of a sample before adsorption takes place. By understanding the graph of absorbance against concentration, you can accurately determine the concentration of a substance and identify potential issues with the measurement.

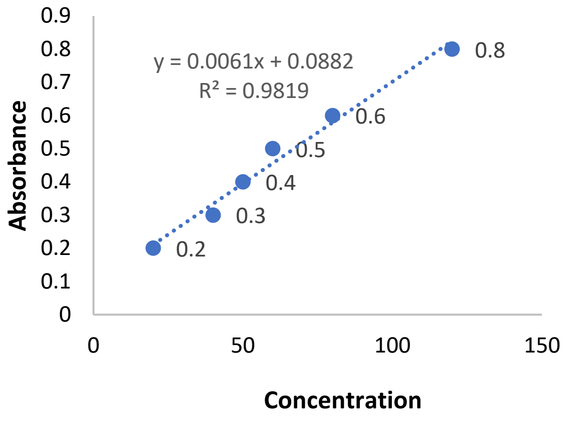

Figure 5. The calibration curve from the result for the initial AAS test before adsorption

The effect of pH on heavy metals removal is a critical aspect of environmental remediation and waste water treatment. Figure 6 dipicts the effect of adsorption with respect to the varying pH values.

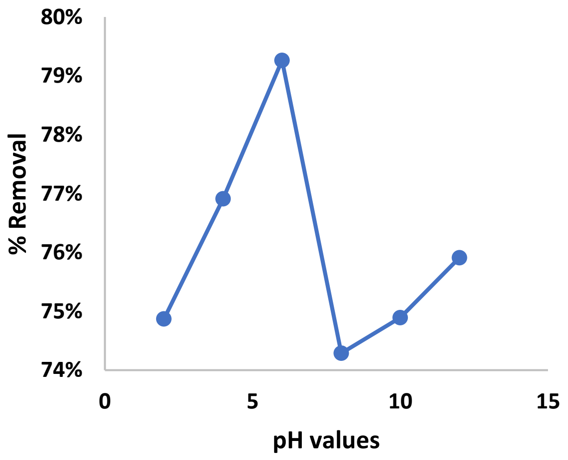

Figure 6. The effect of pH on percentage removal of heavy metals

The effect of pH was investigated for the adsorption of chromium from a solution of potassium dichromate solution of 50 ppm. The pH parameters were varied between the values of 2 and 12 over a wide range of acidic and basic pH regions, with a pH interval of 2(i.e., 2,4,6,8,10,12). A uniform volume of 20mL of 50ppm potassium dichromate solution was measured and added to 0.02g of modified Albizia lebbeck seeds derived activated adsorbent (MALS). The six conical flasks of varying pH values were left inside a water bath at a constant temperature of 25°C and were agitated for 120 minutes. Hence, while all other factors were kept constant the pH values were varied. It was observed that the optimum pH for adsorption was a pH value of 6. This could be attributed due to several factors, including the adsorbate and the surface charge of the adsorbent. The maximum level of percentage removal observed around a pH of 6 is due to charges that attract or facilitate binding of the adsorbate atop the surface of the adsorbent, enhancing the adsorption efficiency.

As the pH increases gradually from 6 and into the basic range, the surface charge of the adsorbent may change. Electrostatic repulsion between the adsorbate and the adsorbent could be a significant factor that accounts for the sharp decline in the percentage removal as it progresses into the basic region. The increase in percentage removal of chromium as the pH value increases from 8 to 12 is as a result of the surface charge of the adsorbent becoming positively charged, reaching a point where it can favourably interact with the adsorbate. As a result of possible changes, the adsorbate could undergo changes in ionization state, leading to improved adsorption efficiency due to more favorable interactions between with the positively charged adsorbent surface.

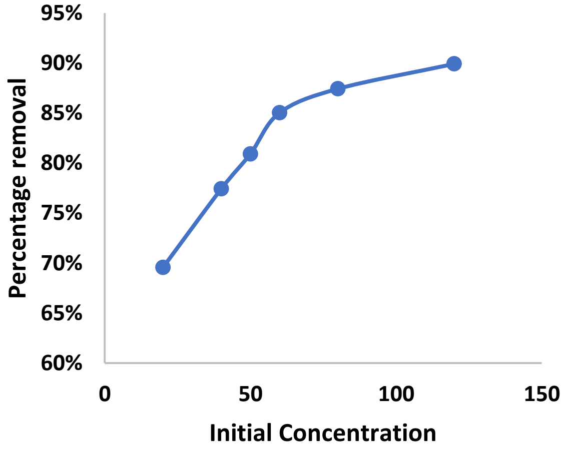

Figure 7. The effect of Initial concentration against percentage removal

The Figure 7 shows the plot that depicts the relationship between the percentage removal and the initial concentration of the solution.Six standard solutions of varying concentrations were prepared using a stock solution of potassium dichromate with concentration of 1000 ppm. The six concentrations were; 120 ppm, 80 ppm, 60 ppm, 50ppm, 40 ppm and 20 ppm. It was observed that the percentage removal of chromium increased with the potassium dichromate solution. It was further observed that equilibrium was approached as the plot progressed towards 120ppm against percentage removal. It has been ascertained from research that adsorption processes generally follow equilibrium kinetics. When the system reaches equilibrium, the percentage removal stabilizes. It can be seen from the plot of initial concentration against percent removal that the percent removal begins to stabilize at around 120ppm. At lower concentrations, it may take longer for the system to reach equilibrium, which can result in a lower percentage removal when compared to higher concentrations where equilibrium is reached more quickly [35]. Another reason for the trend may be attributed to the fact that at lower concentrations, the adsorption sites may not be fully utilized, resulting in a lower percentage removal. As the concentration increases, the adsorption sites become saturated, and the percentage removal approaches a maximum value.

The effect of adsorbent dosage on the percentage removal of chromium from the solution is also a critical parameter in the adsorption processes, as it directly impacts the efficiency of the pollutant. The general increase in the percentage removal as the dosage of the adsorbent increased as shown in Figure 8 can be attributed to the available surface area for adsorption. Adsorption occurs at the surface of the adsorbent, so a greater surface area provides more sites for the target substance to adsorb to. This leads to higher adsorption capacity and, therefore, greater percentage removal [19].

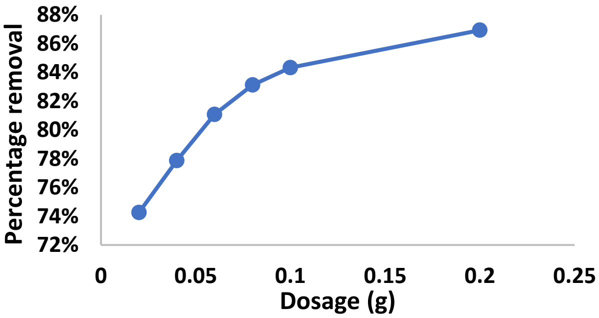

Figure 8. The effect of Absorbent dosage

It is evident that as the dosage increases, more sites become available for adsorption, resulting in increased percentage removal. At lower dosages, some adsorption sites are apparently unoccupied, which may be the resulting factor for limit in the percentage removal. Hence, the maximum adsorption as seen in Figure 8 occurred at an adsorbent dosage of 0.2g.

Effect of time on the removal of heavy metals is also another crucial aspect of adsorption processes. Longer time can lead to higher removal efficiency, as more heavy metal ions are adsorbed. The time required to reach equilibrium varies depending on the adsorbent, initial metal concentration and environmental condition. Figure 9 shows the plot of the removal of chromium from the solution with respect to contact time.The graph result presented showed the removal efficiency of MALS adsorbents increased with an increase in contact time. Equilibrium started to be attained as it approached towards 120 minutes. The increase in the percentage removal may be due to the presence of functional group for long periods being in contact with the adsorbate.

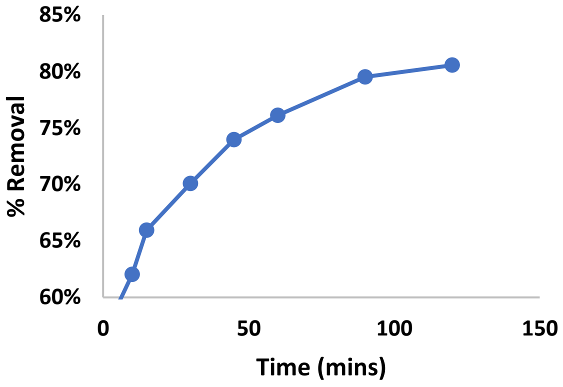

Figure 9. The effect of contact time in the % removal of heavy metals

The effect of temperature on the removal of heavy metals is also of importance in adsorption processes. The factors influencing temperature-dependent removals includes adsorbent type, heavy metal type and the pH and ionic strength. Figure 10 shows the effect og temperature on the adsorption of chromium from the solution.Temperature has strong effect on the intermolecular force between the adsorbate and the adsorbent particles. Effect of temperature on the adsorption process was investigated and the result is as presented in Figure 11. An increase in the temperature causes an increase in the efficiency of MALS removal. This fairly proportional relationship indicated that the adsorption process is an endothermic reaction.

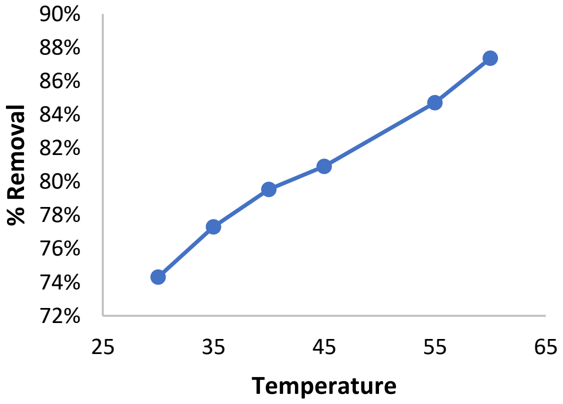

Figure 10. The effects of Temperature in the removal of heavy metals

Mechanism of adsorption refers to the physical and chemical processes that occur when a substance (adsorbate) accumulates on the surface of another substance (adsorbent). When the Potassium dichromate solution came into contact with the activated Albizia adsorbent, it initiated the adsorption process. There were lots of active sites for the chromium ions to interact with the activated adsorbent because of the large surface area [36]. Similar findings have been reported by authors concerning the similar studies on other heavy metals [37].

Physical adsorption, commonly referred to as Van der Waals forces, could be responsible the main initial contact between the chromium ions and the Albizia adsorbent. The attraction interactions between the positively charged chromium ions and the negatively charged adsorbent surface could have caused this weak contact. These chemical reactions depended critically on the existence of oxygen-containing functional groups, such as carboxyl (-COOH), and hydroxyl (-OH), on the Albizia adsorbent surface [38]. Observed a dominant OH species in his biomass which led to high adsorption of X pollutant. This can be referred back to the FTIR studies of the adsorbent which highlighted the presence of these functional groups in the adsorbent [39].

Chemical adsorption was deduced to have been initiated during the course of the experiment when the solution and Albizia adsorbent had more contact time. Compared to physical adsorption, this contact is said to be more focused. Chemical linkages between chromium ions and functional groups that exist on the Albizia surface are possible. For instance, hydroxyl groups and chromium ions can combine to create stable complexes like Cr-OH or Cr-O-Cr given ample time of reaction. The adsorption process is deduced to have reached equilibrium when the rate of adsorption equals the rate of desorption. Adsorption kinetics studies can help determine the rate at which chromium is removed and how long it takes to reach equilibrium [40].

The Adsorption mechanism can be said to be a complex process involving physical and chemical interactions, ion exchange, and electrostatic attraction. Understanding and optimization of these mechanisms was crucial for effective chromium removal during the experiment, which can be attributes to the distinct qualities found in the adsorbent as also found in adsorption studies that involve the removal of heavy metals [32]. The functional groups present, the active sites atop the adsorbent, and the available volume in the various pores are all believed to have played a crucial role in initiating the adsorption process in the removal of chromium from the solution [36].

3.4 Adsorption Isotherms Study

The plots (Figure 11) below illustrate the isotherm studies of the adsorption experiment using the Langmiur and Freundlich isotherms.The experimental model was more suited to the Freundlich model. Experimental data of the chromium removal by activated Albizia seeds adsorbent were successfully fitted using Langmuir and Freundlich isotherms. Table 4 below presents the summary of the data obtained from the isotherms and kinetic studies. The correlation co-efficient (R^2) value for Langmuir was found to be greater than 0.8, but lesser than that of Freundlich with $R^2 > 0.9$ thus, indicating that although both the models can be used to describe the adsorption process the Freundlich model was more suited for the experiment. The 1/n value for Freundlich model was positive, ranging between 0 and 1 implies that the adsorption of chromium onto activated Albizia lebbeck seeds adsorbent was favorable at the studied conditions. The adsorption being more suited to the Freundlich model suggests the formation of heterogeneous multilayers adsorption process is more heterogenous and does not conform to ideal monolayer adsorption assumed by Langmuir model.

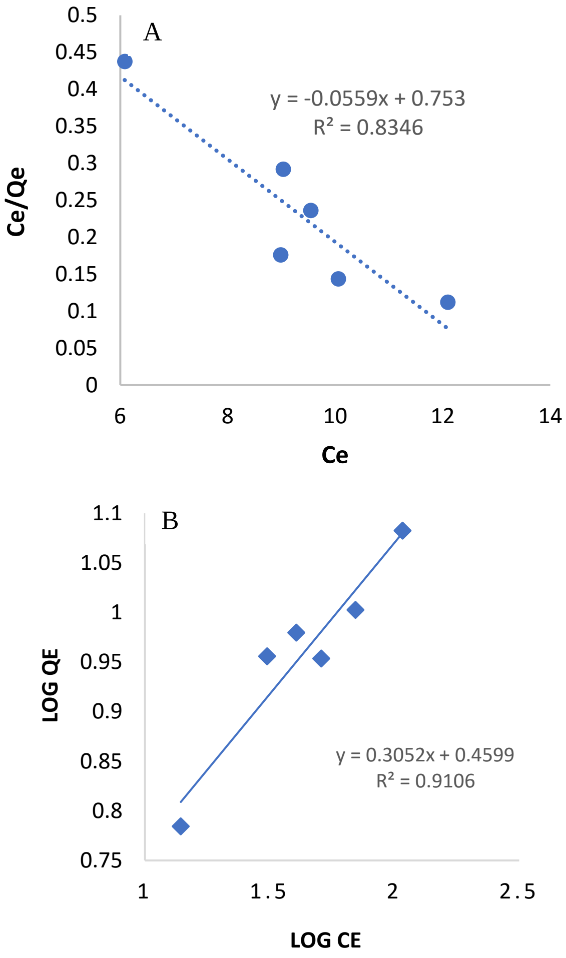

Figure 11. Plot of (A) Langmuir and (B) Freundlich Isotherm model

3.5 Adsorption Kinetic

Figures 12 show the plots of the Pseudo-first and Pseudo-second order. It was observed that the Pseudo-second order kinetics was more suitable for the experimental model [41].The experiment was suitable to both first and second order kinetics, with second order kinetics taking precedence. The kinetics of the adsorption experiment was studied by pseudo-first order and pseudo-second order kinetic models. Data presented in Figure 13b as well as Table 5 showed that the linear correlation coefficient of the pseudo-second-order model (R^2 = 0.991) was minutely higher than the correlation coefficient (R^2) of the pseudo-first-order for (R^2 = 0.986) and. Besides, the calculated Qe (14.718 mg/g) according to the pseudo-second-order model was closer to the experimental Qe (18.344 mg/g), suggesting that the pseudo-second-order kinetic model could better interpret the adsorption behavior. Pseudo-first-order model was also well correlated with predicted in the sense that the R^2 value is also very close to 1, but it has a Qe value that is farther away from the experimentally determined Qe value. As previously known, the pseudo-second-order model suggested that the adsorption process would be the rate-limiting stage in a chemisorption process that involved covalent forces and ion exchange [42]. It also established that the pseudo-second-order kinetic model could more clearly explain the adsorption behaviour, which was consistent with other studies [43].

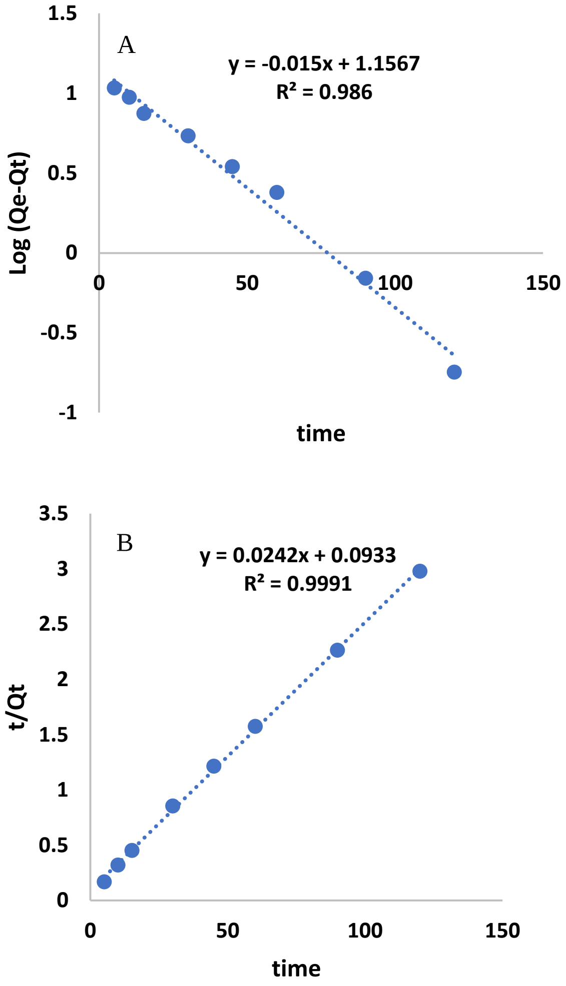

Figure 12. Plot of (A) First Order and (B) Second Oder Adsorption Kinetics

Table 4. The summary of the Isotherm models

Adsorption Models		Chromium removal
Langmuir		
	K_L (L/mg)	-13.47
	Q_{max} (mg/g)	17.889
	R^2	0.8346
	Regression Equation	y = -0.0559x + 0.753
Freundlich		
	K_f (mg/g)	2.8834
	1/n	0.3052
	R^2	0.9106
	Regression Equation	y = 0.3052x + 0.4599

Table 5. Kinetic Model Parameters for removal of chromium

Kinetic Models		Chromium removal
Q_e experimental (mg/g)		18.344
Pseudo-first-order		
	K_1 (min^{-1})	0.015
	Q_e (mg/g)	10.435
	R^2	0.986
	Regression Equation	y = -0.015x + 1.1567
Pseudo-Second-order		
	K_2 (g mg^{-1} min^{-1})	0.0933
	Q_e (mg/g)	14.718
	R^2	0.991
	Regression Equation	y= 0.0242x + 0.0933

3.6 Adsorption Thermodynamics Study

Using the principles of thermodynamics characteristics such change in enthalpy (ΔH°), change in entropy (ΔS°) and change in free energy (ΔG°), the variation in the amount of adsorption with regard to temperature is explained through the relationship obtained from the plot of ln K_d against T^{-1}. The Kd values calculated for the adsorption of chromium is given in Table 6. It was observed that, the Kd values increased with increase in temperature which resulted a shift of equilibrium to the right i.e., it signifies that the adsorption process is favoured, and more molecules are adsorbed onto the solid surface than desorbed from it at the given conditions. The negative values of ΔG° decreased with the rise in temperature; a more negative ΔG indicates that the adsorption process is increasingly favourable at higher temperatures. This implies that the adsorbate molecules have a stronger tendency to be adsorbed onto the solid adsorbent surface as the temperature increases [44].

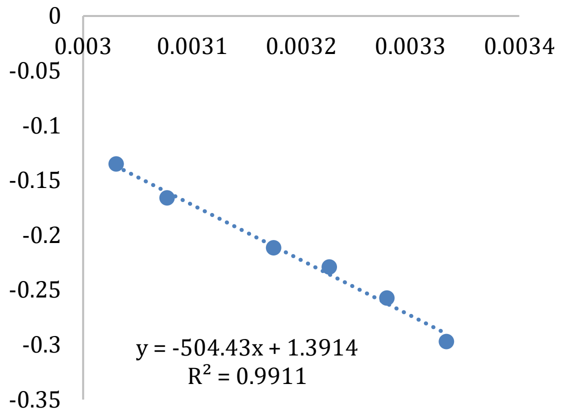

Figure 13. The Thermodynamic study plot of the Adsorption experiment

The negative value of enthalpy (ΔH) as seen in Table 6 typically indicates that the adsorption process is highly exothermic. The ΔH value suggests that the adsorbate molecules are strongly attracted to the adsorbent surface, typically through chemical bonding or strong physical interactions. The strong negative ΔH value is often associated with chemisorption. Chemisorption typically leads to highly stable adsorption, as the adsorbate molecules are bound tightly to the surface [45]. The ΔS (entropy change) value is positive in this adsorption thermodynamics; it suggests that the adsorption process leads to an increase in disorder or randomness in the system as chromium molecules transition from the solution phase to the Albizia adsorbent surface [19].

Table 6. Thermodynamics parameters for adsorption of Chromium

Temperature (°C)	**ΔG° (kJmol^{-1})**	**ΔS° (J K^{-1} mol^{-1})**	**ΔH° (kJ mol^{-1})**	**K$_d$**
30	-7664.26	11.5681	-4193.831	0.74306
35	-7722.10	11.5681	-4193.831	0.7731
40	-7779.94	11.5681	-4193.831	0.79534
45	-7837.78	11.5681	-4193.831	0.80924
55	-7953.46	11.5681	-4193.831	0.84712
60	-8011.30	11.5681	-4193.831	0.87356

4. CONCLUSION

The removal of heavy metals was achieved from this research, characterization studies which include Scanning Electronic Microscopy (SEM), reveals the irregular surface morphology with pore, similarly the Fourier Transform Infrared Spectroscopy (FTIR), identified all the functional groups (hydroxy, carboxyl and amino) while the Brunauer-Emmett-Teller (BET) analysis determine the surface area to volume ratio of the pour space (1023m^2/g and 0.57cm^3/g respectively). Furthermore, the adsorption studies of the Albizia lebbeck seed based investigated the best pH, contact time, and the initial metal concentration, dosage and temperature at pH 6, 120ppm, 0.2g and 60oC respectively. In the same way the physiochemical properties such as bulk density, ash content, and moisture content were obtained with a good performance as compared to other literatures.

The removal of heavy metals from wastewater is a critical environmental concern, and the development of effective sustainable adsorbents is essential. This study demonstrated the potential of Albizia lebbek seed based activated carbon as a low, eco-friendly adsorbent for the removal of heavy metals from wastewater. The results showed that the Albizia Lebbek seed based activated carbon exhibited high adsorption capacities for Cr. Pb (II), Cd (II), and Ni (II) ions with maximum adsorption capacities. The adsorption process was found to be pH- dependent, with optimal removal efficiencies achieved at pH 6.0. The kinetic and equilibrium data were well described by the pseudo first and second order and Langmuir models, respectively. The thermodynamic analysis revealed that the adsorption process was spontaneous and exothermic with **Δ**G ranging from -7664.2609 to 8011.30388 and **Δ**H-4193.831 similarly, 17.718 mg/g and 18.344mg/g for both pseudo first and second order models with Linear correlation of R^2 found to be 0.986 and 0.991 for pseudo first order and pseudo second order respectively. Overall, this study highlights the potential of Albizia Lebbek seed-based activated carbon as a sustainable, effective adsorbent for heavy metals removal from wastewater. Further research needed to scale up to explore its application in real world wastewater treatment scenarios.

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