

**ADSORPTIVE REMOVAL OF LEAD(II) USING
ACTIVATED CARBONACEOUS ADSORBENT OBTAINED
FROM WALLNUT SHELL(*Juglans regia*)**



A DISSERTATION

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BOARD OF EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled “**ADSORPTIVE REMOVAL OF LEAD (II) USING ACTIVATED CARBONACEOUS ADSORBENT OBTAINED FROM (*Juglans regia*) WALNUT SHELL**” by Suresh Timalisina, under the supervision of **Asst. Prof. Dr. Deval Prasad Bhattarai**, Department of Chemistry, Amrit Campus, Thamel, Kathmandu, Nepal is hereby submitted for the partial fulfillment of a Master of Science Degree in Chemistry. This dissertation work has been accepted and forwarded for the award of a degree.

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RECOMMENDATION LETTER

This is to certify that the dissertation entitled “**ADSORPTIVE REMOVAL OF LEAD(II) USING ACTIVATED CARBONACEOUS ADSORBENT OBTAINED FROM (*Juglans regia*) WALNUT SHELL**” has been carried out by Suresh Timalisina (Roll No: 1214/074, TU Regd No: **5-1-33-152-2009**) as partial fulfillment of Master of Science in Chemistry under my supervision. To the best of my knowledge, this work has not been submitted to pursue any other degree in this institution.

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DECLARATION

I, **Suresh Timalisina**, hereby declare that the work presented here is genuine work done originally by me under the supervision of Assistant Professor Dr. Deval Prasad Bhattarai. This dissertation has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data, or work done by others are cited in this dissertation with due acknowledgment and listed in the reference section.



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LIST OF ABBREVIATIONS

CWS	-	Charred walnut shell
XWS	-	Xanthated walnut shell
μm	-	Micrometer
WHO	-	World health organization
XRD	-	X-ray diffraction
FTIR	-	Fourier transform infrared spectroscopic analysis
W	-	Weight of adsorbent in gram
C_i	-	Initial concentration
C_e	-	Equilibrium concentration
K_L	-	Langmuir equilibrium constant (L/g)
K_F	-	Freundlich constant (L/g)
ppm	-	Parts per million
R^2	-	Correlation coefficient
K_1	-	Pseudo-first-order rate constant
K_2	-	Pseudo-second-order rate constant
EDX	-	Energy dispersive X-ray analysis.
XWBL	-	Xanthated walnut shell before adsorption lead metal
XWAL	-	Xanthated walnut shell after adsorption lead metal

ABSTRACT

Presence of heavy metal ions in excess than permissible limit in aquatic environment can cause serious problems to human being and aquatic life. Adsorption is by far the most effective method for the removal of trace amounts of toxic heavy metals from wastewater. The main aim of this thesis work is to prepare a low-cost, effective, and highly efficient adsorbent from the walnut shell by chemical modification for the removal of Pb(II) ions from an aqueous solution. Charred walnut shell (CWS) and xanthated walnut shell (XWS) as adsorbents have been prepared. FTIR, XRD, and SEM characterization are used for the characterization of adsorbents. Batch experiments are performed for analysis. The effect of pH, Pb(II) concentration, and contact time have been investigated using both CWS and XWS adsorbents. The optimum working pH of 4 and optimum time of 150 min are determined for both the adsorbents. Equilibrium sorption data are best fitted for the Langmuir isotherm model and the maximum adsorption capacity of CWS and XWS are found to be 61 mg/g and 109.9 mg/g, respectively. Kinetic modeling studies revealed that the experimental data best fit to pseudo-second-order kinetic model. These results demonstrate that XWS may be an attractive alternative bio-adsorbent for the removal of Pb(II) from an aqueous solution

Keywords: walnut shell, adsorbents, CWS, XWS, lead ion, Langmuir Isotherm

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CHAPTER-1

INTRODUCTION

1.1 Heavy Metals

Heavy metals do not have a unanimous definition but they are a member of a loosely-defined subset of elements that exhibit metallic properties. Heavy metals are the group of metals and metalloids with high atomic weight and an atomic density greater than 4 g/cm³. Heavy metals mainly include transition metals, some metalloids, lanthanides, and actinides. Not all but some of them may be toxic even at very low concentrations [1]. Heavy metals like lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), etc. are natural components of the Earth's crust and can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater [2]. The presence of heavy metals in the environment has a great concern due to their increasing discharge, toxic nature, and other adverse effects into receiving water bodies and thereby affecting significantly the quality of water [3].

Metals like cobalt, iron, zinc, etc. are needed at low level for human for enzyme activities but excessive exposure can result in toxicity. These metals can cause serious health effects with varied symptoms depending on the nature and quantity of the metal ingested [4], as well as the age, route of exposure, gender, genetics, and nutritional status of the exposed individual. In effect, these heavy metal ions may damage or reduce mental and central nervous function, lower the energy levels, cause irregularity in blood composition, and affect vital organs such as kidneys and liver [5]. These metals cannot be degraded or detoxified readily and tend to accumulate in living organisms causing various diseases and disorders. Heavy metals like lead, copper, cadmium, etc. in water are hazardous to an environment that is directly related to human beings as well as environments. That's why this research is important [6].

1.2 Lead and Toxic Ion

Lead is symbolized by Pb with an atomic weight of 207.19 and atomic number of 82. It is placed in group 14 (IVA) of the periodic table. Its melting point is 327.5 °C and its density is 11.34 g/cm³. Lead is one of the most toxic heavy metals generally found

in three oxidation states i.e., Pb, Pb²⁺, and Pb⁴⁺. It is easily accumulated in living organisms via different route but hard to degrade into nontoxic end products. According to Nepal's drinking water quality standards, the highest permissible limit of lead in drinking water is 0.05 mg/L (25 ppb) and according to WHO guidelines for drinking water quality, the permissible limit for Pb(II) is 0.01 mg/L (10 ppb) [9]. Lead is a soft, highly malleable, and flexible metal that has excellent corrosion resistance properties [10]. Pb is highly used in textile dyeing, ceramic and glass production, petroleum refining, battery production, and mining [8]. Lead is not toxic in its metallic form until and unless, it is acted upon by intestinal secretion. Soluble salts of lead are easily assimilated into the blood stream and acts as cumulative poisoning. It is presumed that toxic impact of lead is due to increased production of reactive oxygen species (Bandyopadhyay et al., 2014). Lead (IV) is formed only under extremely drastic condition. Therefore, toxicity concern about lead is mainly due to Pb(II).

1.3 Sources of Lead Contamination

Lead has a wide range of applications in different industries, the largest of which is in the manufacture of storage batteries [11]. Because of its versatility, lead is used in weaponry for making bullets and shots, scuba diving weight belts and ballast keel of sailboats, coloring pigments in paints and ceramic glazes, soldering material, sheathing and insulating material to cover electrical wirings, and as a coolant for certain nuclear reactors. The use of Pb is not only limited to these applications but also used in the construction industry for cladding and roofing to avoid water penetration, in the glass of computer and television screens as radiation shielding material, as protective shielding around nuclear reactors and containers used for storing radioactive materials, and as an anti-knock additive in the fuel to improve vehicle performance [11, 12].

Lead as Pb (II) is released into the environment from aforementioned applications and other various industrial processes: industries engaged in lead-acid batteries, pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials, explosive manufacturing, ceramics, glass, paint, oil, metal, phosphate fertilizer, electronics, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater, sea spray and many more. Not

only leaded gasoline causes lead concentrations in the environment to rise but also human activities such as fuel combustion, industrial processes, and solid waste combustion, also contribute in the lead contamination.

1.4 Health impact and environmental aspect of Lead

Lead is one out of four metals (Cd, Hg, As, Pb) that have the most detrimental effects on human health. Lead poisoning is also known as plumbism and saturnism. Lead can enter the human body via ingestion, inhalation, and skin absorption. For those people who are involved in occupations such as painting and decorating, plumbing, construction work, and car repair, are exposed to higher levels of lead from their work environment [13]. Lead can have devastating consequences for the health of children. At a high levels of exposure, lead attack the brain and central nervous system to cause coma, convulsions, and even death. Children who survive severe lead poisoning may be left with mental retardation and behavioral disorders. In particular, lead affects children's brain development resulting in reduced intelligence quotient (IQ), behavioral changes such as reduced attention span and increased antisocial behavior, and reduced educational attainment. Lead exposure also causes anemia, hypertension, renal impairment, immune toxicity, and toxicity to the reproductive organs. The neurological and behavioral effects of lead are believed to be irreversible. At lower levels of exposure lead causes no obvious symptoms but it is known that, as lead exposure increases, the range and severity of symptoms and effects also increases. Even blood lead concentrations as low as 5 $\mu\text{g}/\text{dl}$, once thought to be a "safe level", may result in decreased intelligence in children, behavioral difficulties, and learning problems. Various detrimental effects of lead are as follows:

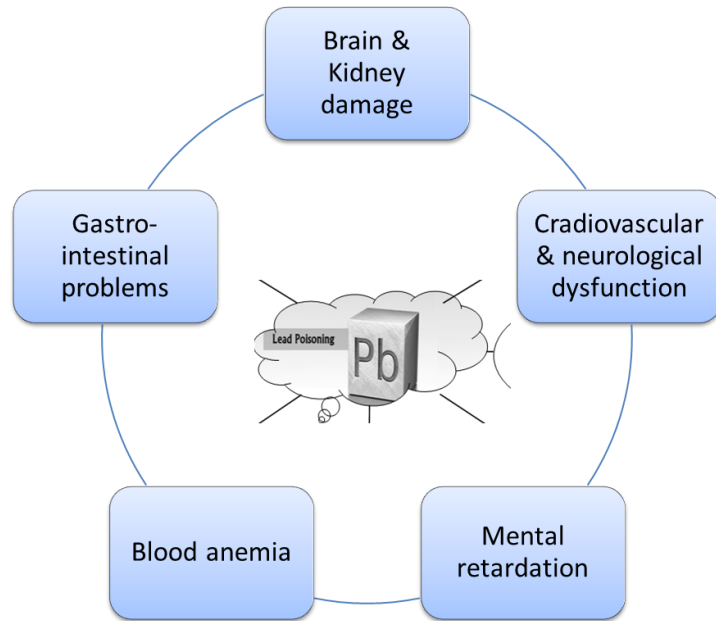


Figure 1: Health impacts of lead exposure.

1.5 Lead Contamination in Nepal

The Himalayan region of Nepal contains rocks and minerals associated with lead and flat plain areas in the southern belt of Nepal's, Terai region, possesses a strong possibility for high lead content in the groundwater [13]. In Nepal, lead (Pb) contamination in drinking water is a major concern and has recently become one of the major environmental health management issues, especially in the plains region, i.e., in the Terai districts, where the population density is relatively high. The Terai inhabitants still rely on groundwater for their daily water requirements, including drinking water and other agricultural purposes [14].

The districts Nawalparasi, Bara, Parsa, Rautahat, Rupandehi, and Kapalivastu are among the regions in the lowlands (Terai) of Nepal most severely affected by the lead contamination [15]. Although, World Health Organization (WHO) had lowered the baseline of lead 10 micrograms per decilitre ($\mu\text{g}/\text{dL}$) safe limit due to widespread negative health effects on humans [15]. Therefore, the removal of Pb(II) from drinking water is essential for the protection of human health and the environment, and hence the recovery and removal of Pb (II) from wastewater has become a major topic of research in water treatment [9].

1.6 Methods for Removal of Lead

Lead contamination of groundwater in different parts of the world is an outcome of various natural and anthropogenic sources which become the greatest threats to human health and environment. Therefore, removal of lead is very essential. There are several methods for the removal of lead from an aqueous solution. Some conventionally applied techniques to remove lead species include;

- **Oxidation / Reduction:** Oxidation or reduction process alters the chemical form of lead by reducing or oxidizing chemicals thereby optimizing other processes.
- **Adsorption:** It uses various types of adsorbents at the surface of metal ions that accumulate and remove.
- **Ion exchange:** It is similar to adsorption process, but the medium is a synthetic resin of a more well-defined ion exchange capacity.
- **Coagulation / Flocculation:** This method uses coagulant to form gelatinous mass to trap lead particles which then can be settled and removed by sedimentation or filtration.
- **Bioremediation:** It uses the most efficient plant that can remove contamination from water by adsorption through the roots.
- **Precipitation:** In this method, dissolved metal ions get precipitated by chemical reagents (precipitants) and result in the formation of metal hydroxides, sulfides, carbonates, and phosphates (insoluble solid particles) that can be simply separated by sedimentation or filtration.
- **Membrane techniques:** This process uses selectively permeable membrane which acts as a molecular filter and removes dissolved lead compounds.

All of the above mentioned methods have been used for the effective removal of lead from an aqueous solution. However, these techniques have some limitations such as low efficiency, sensitive operating condition, and the production of secondary sludge, which increases the cost [16, 17]. Adsorption, as compared to the different conventional methods, appears to be more attractive due to its high efficiency, cost-effectiveness, and reversible nature as adsorbent materials can be regenerated by desorption of the adsorbed metals for multiple reuses [6].

Agricultural by-products are of particular interest since these materials are produced in great amounts, can be produced as per requirement and are easily available worldwide. Agricultural waste material (or their derivatives) could be very efficient bio-sorbent for metal removal as it is composed of cellulose, hemicellulose, and lignin having good abilities to adsorb heavy metals. The main advantage of agricultural waste products over other conventional adsorbents is their strong affinity and high selectivity towards heavy metals due to the abundant availability of binding groups on their surface [7].

Therefore, for the developing country like Nepal adsorption is considered as an economical and effective technique for the removal of lead due to its lower cost, and availability of suitable adsorbents and their regeneration. Activated carbon is being used as an adsorbent in most industrial systems for the removal of metals in wastewater attributable to its notable adsorption capability. Activated carbon is already a very important industrial raw material. Many agricultural by-products and animal wastes have been used as sources for activated carbon, such as date stone, walnut shell, corn corb, pistachio shells, cassava peel, olive cake, cow dung, orange peel, nutshell, sawdust, etc. To increase the efficacy of these conventional and costly techniques, adsorption on activated charcoal plays a vital role in wastewater treatment. The bio-adsorbent material is locally available and is cheap, so they are cost-effective too. Also, it is a powerful and well-established technique that requires no more initial operational cost and no problem for sludge disposal. Therefore, through this research work, the potential of one more new waste matter walnut shell which is accessible in abundance in Nepal has been explored in this study.

1.7 Adsorption Study

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid (adsorbate) to a surface (adsorbent) [18]. Adsorption occurs naturally in physical, biological, and chemical systems, but industrialists have perfected adsorption methods to clean up hazardous waste in wastewater or purify drinking water. Adsorption is superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants [19]. Adsorption can be classified into two types, which are physisorption and chemisorption, both differ like bonding. The difference between physisorption and chemisorptions is listed in Table below;

Table 1: Difference between Physisorption and Chemisorption.

Physisorption	Chemisorption
The operating forces are weak van der Waals' forces.	The operating forces are chemical bonds.
No compound formation takes place.	Surface compounds are formed
The process is reversible i.e. desorption occurs by increasing temperature or decreasing pressure.	The process is irreversible. Efforts to free the adsorbed adsorbate give some definite compound.
It does not require any activation energy.	It requires activation energy.
Adsorption decreases with increase of temperature.	Adsorption first increases with increase in temperature. The effect is called activated adsorption.
It is not very specific in nature. i.e. all adsorbate are adsorbed on all adsorbent to some extent.	It is highly specific in nature and occurs only when there is some possibility of compound formation between adsorbate and adsorbent.
It may form multi-molecular layer.	It forms uni-molecular layer.
Heat of adsorption is low i.e. in range of 20-40 kJ/mol.	Heat of adsorption is high i.e. in the range of 50-400 kJ/mol.

Adsorption is a surface phenomenon at a given temperature and pressure which depends on the surface area of the adsorbent [22]. Physical adsorption i.e., physisorption is due to weak van der Waals forces between adsorbate and adsorbent whereas chemical adsorption i.e., chemisorption is due to strong chemical forces of bonding type between adsorbate and adsorbent [23]. The adsorption can be studied in the following ways:

1.7.1. Batch Adsorption Method

Batch adsorption is performed to evaluate the adsorption isotherms of metal ions onto the surface of the adsorbent. In batch adsorption method, a known amount of adsorbent is mixed with the required volume of solvent, concentration and pH of the solution is adjusted followed by continuous agitation at room temperature for 24 hours in a mechanical shaker to reach adsorption equilibrium. Initial and equilibrium concentration of metal ions are determined by some suitable approach (e.g., AAS) to evaluate the extent of adsorption. Adsorption of Pb(II) on different adsorbents is influenced by various parameters such as pH of the solution, initial concentration of the arsenic solution, contact time, and adsorbent dose. Thus, to understand the mechanism and effectiveness of adsorption one of the parameter is changed, keeping other parameters constant [24]. The amount of metal adsorbed at equilibrium per unit mass is calculated as

$$q = \frac{C_i - C_e}{W} \times V \quad (1)$$

Where ‘ C_i ’ is the initial concentration ‘ C_e ’ is the equilibrium concentration, ‘ V ’ is the volume of adsorbate solution in milliliter and ‘ W ’ is the weight of adsorbent in milligram.

The percent of metal ion adsorption (%A) is calculated using the equation [25].

$$A\% = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

1.7.2. Column Adsorption Method

In the column adsorption method, a column of particular internal diameter and length is set up to determine the effect of operating parameters such as flow rate, bed depth, pH, and concentration. Glass wool is kept at the bottom of the column to improve the flow distribution and prevent the loss of adsorbent. The effluent is allowed to flow through the column at a constant flow rate using a flow controller. Effluent samples are collected from the exit of the column at different time intervals and are used for pH and arsenic concentration measurement. The experiment continues until the concentration at the outlet of the column almost equals the concentration at the inlet. The metal concentration before and after adsorption is measured which helps to evaluate the efficiency of adsorbent in the column [26].

1.8 *Juglan regia* as Bioadsorbent

Juglan regia, commonly called 'walnut', and "Okhar" in Nepali. Walnut is a drupe nut, that belongs to *Juglandaceae* family is distributed in Nepal, China, the United States, and Eastern Europe. The outer skin of raw walnut is a hard, heavy, and brown color shell. The underside of walnut fruit is a sweet, tasty, and edible nut. Walnut nutrition is beneficial for human health and an excellent source of carbohydrates, protein, vitamin C, dietary fibers, fat, and many important vitamin B-complex groups. It has been studied that walnut extracts have antimicrobial, antioxidant, and antibacterial properties which suggested that they can potentially improve human health. Walnut wood has high tannin content and is used to obtain waterproof leather. The raw and modified forms of walnuts have proved their excellent adsorptive capability towards thallium, heavy metal ions, organic compounds, and dyes [20].



Figure 2: Walnut Shell (*Juglan regia*)

Bio-adsorption is a complex process, mainly comprising of ion exchange, chelation, and adsorption by physical forces and entrapment in inter and intra-fibrillar capillaries and space of the structural polysaccharide network as a result of the concentration gradient and diffusion. Bio-adsorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or Physico-chemical pathways of uptake. Algae, bacteria and fungi, and yeasts have proved to be potential metal bio sorbents [21]. The major advantages of biosorption over conventional treatment methods include cost-effective, highly efficient, no additional nutrient required, minimum chemical or biological sludge, regeneration of biosorbent, and possibility of metal recovery.

1.9 Enhancement of bio-adsorbent

Bio-waste collected is converted into carbon by the chemical treatments adding concentrated Sulphuric acid. The charred bio-waste can be further activated by chemical modification. Activation of the surface functional group, rate adsorption increases gradually.

1.10 Adsorption Isotherms

The surface coverage of adsorbate is the function of adsorptive adsorbents, so sorption isotherm describes the equilibrium of the sorption of material at a surface at a constant temperature. It represents the amount of material bound at the surface as a function of material present in a gas phase or the solution. Sorption isotherms are used in empirical models frequently used models are Freundlich isotherm and Langmuir isotherm.

1.10.1 Langmuir Adsorption Isotherm

It is a semi-empirical isotherm derived from the proposed kinetic mechanism. The Langmuir isotherm is the best known of all isotherm describing sorption and it has been successfully applied to many sorption processes based on the surface of adsorbent is uniform that all adsorption sites are equivalent, adsorbed molecules do not interact with each other, all the adsorption occur through the same mechanism and at the maximum adsorption only a monolayer is formed. Molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, instead, that adsorption occurs only on the free surface of the adsorbent.

$$\frac{1}{q_c} = \frac{1}{q_m b c_e} + \frac{1}{q_m} \quad (3)$$

Or,

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \quad (4)$$

Where q_e = amount of metal ion adsorbed per unit weight of adsorbent (mg/g)

c_e = Equilibrium concentration of the adsorbate in a solution after adsorption (mg/L)

q_m = Langmuir constant related to monolayer sorption.

b = Langmuir constant related to the equilibrium constant and represents enthalpy of sorption. The standard slope of $\frac{c_e}{q_e}$ Vs $\frac{1}{q_m}$ gives the value of $\frac{1}{b}$ from which the value of b can be determined. The intercept gives the value of $\frac{c_e}{q_m}$ from which the value of q_m can be determined.

As with all the chemical reactions, the equilibrium constant b is both temperatures dependent and is related to Gibb's free energy and hence to the enthalpy change of the process.

$$G^\circ = RT \ln b \quad (5)$$

Where, R = universal gas constant in $J K^{-1} mol^{-1}$. And Langmuir parameter K_L which is given by the following equation

$$K_L = \frac{1}{1 + bC_o} \quad (6)$$

If $K_L=1$ linear and C_o = initial concentration of adsorbate (mg/L)

And $K_L= 0$ indicates the shape and nature of the adsorption process.

If $K_L > 1$, unfavorable, $K_L < 1$, favorable and $K_L= 0$ indicates an irreversible type of adsorption.

1.10.2 Freundlich Adsorption Isotherm

In 1909 Freundlich gave an empirical relationship representing an isothermal variation of quantity of adsorbate adsorbed by unit mass of adsorbent with pressure, i.e. this process is known as Freundlich adsorption isotherm equation.

$$q_e = \frac{Kc_e}{n} \quad (7)$$

$$\text{or, } \log q_e = \log K + \frac{1}{n} \log c_e \quad (8)$$

Where q_e = amount of adsorbed per unit weight of adsorbent (mg/g)

c_e = equilibrium concentration in (mg/L)

K = adsorption constant roughly gives adsorption capacity (mg/g)

n = Freundlich constant characteristic of adsorption system

Plot of $\log q_e$ Vs c_e gives a straight line with an intercept of $\log K$ and slope of $\frac{1}{n}$. Experimentally, it was found that the exact of adsorption varies directly with pressure till a saturation pressure is reached beyond that point, rate of the adsorption saturates even after applying higher pressure. The value of $\frac{1}{n}$ lies between 0 to 1 and indicates the favorable adsorption of metal ions. This isotherm does not predict any saturation of the sorbent by the sorbet. Thus infinite surface coverage is predicted mathematically indicating multilayer adsorption on the surface. So apart from homogenous surface adsorption is also suitable for a highly non-ideal sorption that involves a heterogeneous surface.

Sorption studies can be conducted by the batch technique. Batch experiments are carried out to determine the adsorption kinetics of metal ions onto the adsorbents in a reagent bottle. The reagent bottles were shaken at a constant rate, allowing sufficient time for adsorption equilibrium. It is assumed that the applied shaking speed allows all the surface area to come in contact with heavy metal ions throughout the experiments. The study can be performed at room temperature to be representative of environmentally relevant conditions. The pH of the solution is measured with a pH meter. The reagent bottles will be plugged and kept closed to avoid the fluctuation of pH due to the exchange of gases during the experiment. The effects of various parameters on the rate of the adsorption process will be observed by varying contact time, adsorbent concentration, temperature, and pH of the solution [23]. Keeping one parameter changing and another parameter constant, the effect of each parameter can be studied. The solution volume (V) is kept constant. The amount of metal adsorbed per unit mass is calculated by using formula as,

$$q_t = \frac{C_i - C_e}{w} \times V \quad (9)$$

Where C_i and C_e is the initial and equilibrium concentration (mg/L) is the mass of the adsorbent (g) and V is the total volume of the solution taken (mL). Removal of lead ions in percentage (R) was calculated by using the relation as;

$$R\% = \frac{C_i - C_e}{w} \times 100 \quad (10)$$

1.11 Adsorption kinetics

The study of adsorption kinetics in waste water treatment is important as it not only provides valuable insight into the reaction pathways and the mechanism of sorption reactions but also describes the solute uptake rate, which in turn controls the residence time of sorbate uptake at the solid-solution interface [27]. The kinetics data obtained from adsorption of Pb(II) ions onto walnut shell (*Juglans regia*) can be studied by using two common kinetic models, which are the pseudo-first-order kinetic model and pseudo-second-order kinetic model. The best fit model is selected based on the linear regression correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data.

1.11.1 Pseudo-first order kinetic model

To distinguish kinetics of equation based on the sorption capacity of solid form, concentration of solution, Lagergren's first-order rate equation (1898) has been called pseudo-first-order kinetic model. The pseudo-first-order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first-order equation is expressed as,

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (11)$$

Where, q_e = amount of metal adsorbed at equilibrium (mg/g)

q_t = amount of metal ion adsorbed at any time (mg/g)

K_1 = Lagergren's rate constant for first-order adsorption (min^{-1})

On integrating, the equation becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (12)$$

The plot of $\log(q_e - q_t)$ versus t gives a straight line from which K_1 and q_e can be determined from slope and point of interception, respectively.

Hence,

$$K_1 = -\text{slope} \times 2.303 \quad (13)$$

$$q_e = C \quad (14)$$

1.10.2 Pseudo-second order kinetic model

The pseudo-second-order is based on the assumption that the rate-limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between heavy metal ions and adsorbent. The pseudo-second-order kinetic rate equation is expressed as [25]

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (15)$$

Integrating this equation at boundary condition gives,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (16)$$

$$\text{Let, } P = K_2 q_e^2 \quad (17)$$

$$\frac{t}{q_t} = \frac{1}{P} + \frac{1}{q_e} \times t \quad (18)$$

The linear plot of $\frac{t}{q_t}$ versus t gives values of q_e and K_2 . The validity of kinetic models can be investigated by studying the kinetics at different time intervals. The equilibrium uptake of metal should be equal to the experimental equilibrium. If it is not so, the reaction is not likely to follow the model [28].

1.12 Calibration Curve

A calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. The calibration curve is based on Beer-Lamberts law which states that there is a linear relationship between the absorbance and concentration of a sample. For AAS analysis, the validity of Beer-Lambert law is tested by plotting a calibration curve which should give a straight line passing through the origin.

Beer-Lambert law is written as:

$$A = \epsilon l C \quad (19)$$

Where 'A' is the measure of absorbance, ' ϵ ' is the molar absorption coefficient, ' l ' is the path length and ' C ' is molar concentration. The molar absorption coefficient is given as a constant and varies for each molecule. The standard spectrometer uses a

cuvette that is 1 cm in width, l is always assumed to be 1 cm. Since absorbance, molar absorption coefficient, and path length is known, we can calculate the concentration 'C' of the sample.

CHAPTER- 2

OBJECTIVE OF THE STUDY

In this research, chemically activated bio-adsorbent (Walnut shell) were prepared as one of the best and economic ways for the removal of lead (II). The objective of the study is categorized into two parts:

2.1 General objective

The general objective of this research work is the preparation of bio-adsorbent from walnut shell bio-waste followed by chemical modification to charred and xanthate forms for investigating the adsorption capacity to remove of lead as heavy metals.

2.2 Specific objectives

1. Preparation of powdered form of a walnut shell.
2. Charing of walnut shell using conc. sulphuric acid to charred form.
3. Xanthation of charred walnut shell powder with KOH and CS₂.
4. Characterization of adsorbent using SEM and FTIR for adsorptive removal of lead from aqueous solution.
5. Determination of various physicochemical controlling factors affecting adsorption including pH, initial concentration, and contact time.
6. Kinetics and isotherm model study for adsorption process.

2.3 Research gap and novelty of the work

Different conventional methods are available for the removal of lead but these processes are costly and not eco-friendly which may not be suitable for developing countries like Nepal. Adsorption using agro-wastes is one of the most widely used methods because of its abundant availability and low-cost owing to relatively high carbon content and presence of porous structure. We developed a new cheap, effective, and promising material to fulfill this research gap by using a low-cost adsorbent prepared from walnut shell waste. Several types of agricultural biomass and fruits shell or peels were used as adsorbent for lead removal in the literature. To the best of our knowledge, chemically activated, Xanthated and Charred bio-adsorbent

walnut shell is a new material that is not studied yet for the preparation of adsorbent for the removal of Pb(II) from aqueous solution.

CHAPTER- 3

LITERATURE REVIEW

Heavy metals are non-degradable and are likely to cause various diseases and disorders through bioaccumulation. Lead, which is one of the priority toxic pollutants, can reach the environment from various anthropogenic sources as well as via natural geochemical processes. Lead is hazardous to the health of diverse animals and is necessary to be removed. The increasing risk of arsenic carcinogenicity for developing countries has drawn the attention of researchers to do more research on lead contamination and treatment for its removal. Different techniques such as coagulation, chemical oxidation, chemical precipitation, ion exchange, membrane filtration, adsorption, and reverse osmosis for reducing the concentration of arsenic in aqueous solutions are available. Some of the mentioned techniques require extremely high investment and operation costs and produce high levels of waste, which in turn makes their treatment and disposal problematic. However, the adsorption process has an extensive application due to the ease of exploitation, high efficiency, and insensitivity.

Kamar and his co-workers,(2015) studied the removal of lead and cadmium ions from aqueous solution using walnut shells as low-cost adsorbent materials by batch adsorption method. An investigation was carried out to identify the effect of pH, initial concentration of the heavy metal ions, contact time, dose, and size diameter of adsorbent on the removal efficiency at 25 °C. Isotherm adsorption parameters were determined by using both Langmuir and Freundlich models. It followed the pseudo-second-order model [28].

In the study of Ashfaq & Ali,(2017), the batch studies showed that Roasted China Clay (RCC) is a potential low-cost, and frequently available adsorbent that can be used to remove Pb(II) ions from aqueous solution. Adsorption of lead on RCC is a fast process as equilibrium was established within 60 minutes. Adsorption of Pb(II) is a pH-dependent and the maximum amount of Pb(II) (96.7%) can be removed from aqueous solution at pH ranging 4-6 at concentration 50 mg/L. Kinetic data also suggest the applicability of both pseudo-first and pseudo second-order model as indicated by the values of correlation coefficients ($R^2 = 0.997$ and 0.998) which also confirms that adsorption of Pb(II) on RCC involve physical process followed by the

chemisorption of adsorbate molecules [29].

Homagai *et al.*, (2010) studied the adsorption capacity of charred xanthated sugarcane bagasse (CXSB) for the removal of heavy metals. The bio-sorbent was characterized by FTIR and elemental analysis. The equilibrium sorption data were fitted well with the Langmuir isotherm model and adsorbent- adsorbate kinetics exhibited a pseudo-second order model. Result analysis of kinetics and calculation of adsorption capacity indicated that CXSB can be used as the selective adsorbent for the removal of different metal ions from wastewater [30].

Yang, *et al.*, (2016), investigated that the biological sludge was used as a low-cost feedstock to prepare adsorbents through ferric activation for the removal of Pb^{2+} ions. The results indicated that ferric-activated SBA showed a well-developed pore structure and enhanced Pb^{2+} adsorption ability, with an adsorption capacity of 42.96 mg/g. The mechanism of Pb^{2+} ions removal by the adsorbents involved ion exchange, precipitation, and surface complexation. The increased surface area and iron compounds of ferric-activated SBA promoted the removal of Pb^{2+} ions. Ferric-activated SBA produced from biological sludge could be used for removing Pb^{2+} ions from water, and it was beneficial to sludge reuse [31].

Shi *et al.*, (2016), investigated that *J. curcas* seed husk ash, which is widely available at low cost, can be used as an efficient biosorbent material for the removal of Pb(II) from wastewater. The amount of Pb(II) removed using *J. curcas* seed husk ash increased with increasing initial pH, contact time, and initial Pb(II) concentration. The removal rate was high for the first 45 min and controlled by internal diffusion, and the sorption process followed pseudo-second-order rate kinetics. The variable-temperature equilibrium data were fitted to the Langmuir adsorption model. The maximum adsorption capacity of the husk ash was 263.10 mg g^{-1} at 298 K at pH 5.0 [32].

Raikar *et al.*, (2015), have investigated the removal of Lead(II) from aqueous solution by using activated and un-activated rice husk. Through chemical activation of the adsorbent, the percentage removal efficiency of an adsorbent can be increased. Hence, activated rice husk shows greater efficiency than un-activated rice husk. Highest percentage lead removal with adsorbent RH (natural un-activated form) was found to be 93.36% at pH 4-5, initial concentration of lead 30 mg/L, contact time of 60

minutes and adsorbent dosage of 1 gram. When RHA (rice husk ash acquired after carbonizing rice husk without pretreatment) is used, the maximum percentage removal is found as 94.8% at pH 4-5, initial concentration of lead 20 mg/L, contact time of 60 minutes, adsorbent dosage of 1 gram. However, with PRH (rice husk pretreated with phosphoric acid), the highest percentage removal of lead is 96.72% at pH 5-6, initial concentration of lead 10 mg/L, contact time of 60 minutes and adsorbent dosage of 4 g. Similarly, for ARH (rice husk pretreated with acetic acid), the maximum lead removal is found to be 99.35% at pH 5-6, initial concentration of lead solution 10 mg/L, contact time of 60 minutes, and adsorbent dosage of 4 g. Rice husk and rice husk ash follow pseudo-second-order kinetics [33].

Lebkiri *et al.*, (2014) studied the removal of lead ions from aqueous solutions by the sugarcane bagasse (SCB). The volume treated for each solution is equal to 100 mL. The kinetic study of Pb^{+2} by the SCB at pH = 5.5 showed that the extraction process is expressed by the kinetic law of second-order, and the extraction equilibrium is reached after 35 min. The pH of the aqueous solution of Pb^{+2} decreases in the course of extraction by the SCB, which is due to the release of the H^+ protons by the sugarcane bagasse in the aqueous solution. In the operating conditions used, the maximum capacity of fixing of lead by SCB is about 3.32 mg/g. The treatment of a mixture of divalent metals containing the Pb, Co, Cd, Cu, and Zn by the SCB, shows that the SCB presents the sequence of the following selectivity: $Pb^{+2} > Cd^{+2} > Zn^{+2} > Cu^{+2} > Co^{+2}$. In the experimental conditions used, a mass of 0.8 g of sugarcane bagasse was found enough sufficient to purify a metallic solution of lead of concentration equal to 20 ppm [34].

Chigondo *et al.*, (2013), studied the adsorptive behavior of lead (II) and copper (II) ions on baobab fruit shells. The study has demonstrated that baobab fruit shells have favorable properties for the bio-sorption of lead and copper ions from aqueous solutions and the adsorbent properties are enhanced by acid treatment. The bio-sorption of lead and copper ions was highly dependent on experimental parameters such as contact time, initial metal concentration, pH, and adsorbent dosage. The adsorption of Pb(II) was found to be optimum at pH 5.5, adsorbent dose of 0.7 g, metal ion concentration of 10 ppm, and contact time of 120 min. The adsorption of Cu (II) was found to be optimum at pH 6, adsorbent dose of 0.9 g, metal ion concentration of 20 ppm and contact time of 120 min. This could be a cost-effective

method of utilizing waste baobab fruit shells in removing lead and copper from industrial wastewater [35].

Meski *et al.*, (2011), investigated the adsorption was greatly pH-dependent, with a high uptake of lead at pH 3. Carbonate hydroxyapatite (CHAP) was synthesized from domestic hen egg shells. The obtained CHAP was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy and investigated as metal adsorption for Pb^{2+} from aqueous solutions. The effect of various parameters on the adsorption process such as contact time, solution pH, and the temperature was studied to optimize the conditions for maximum adsorption. The results showed that the removal efficiency of Pb^{2+} by carbonate hydroxyapatite claimed at 600 °C (CHAPF) reached 99.78%, with an initial Pb^{2+} concentration of 200 mgL^{-1} , pH) 3, and a solid/liquid ratio of 1 gL^{-1} [36].

Kamar *et al.* (2010), studied the treatment of rubber leaf powder with potassium permanganate followed by sodium carbonate, and its performance in the removal of Pb(II) ions from aqueous solution was evaluated. The interactions between Pb(II) ions and functional groups on the adsorbent surface were confirmed by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) coupled with X-ray energy dispersive spectroscopy (EDX). The optimum pH range for lead adsorption was 4–5. Even at a very low adsorbent dosage of 0.02 g, almost 100% of Pb(II) ions (23 mg/L) could be removed. The adsorption capacity was also dependent on lead concentration and contact time, and relatively a short period (60–90 min) was required to reach equilibrium. Kinetic models including pseudo-first-order and pseudo-second-order were used to analyze the lead adsorption process, and the results showed that the pseudo-second-order fitted well with a correlation coefficient greater than 0.99 [37].

Kazemipour *et al.*,(2008), investigated the adsorption of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. The activated carbons produced from shells and stones have high surface areas. Time and temperature of carbonization influenced Cu adsorption. The aqueous adsorption tests indicate that the activated carbon has a notable adsorption capacity for Cu, Zn, Cd, and Pb. The uptake of the Cu was greatly affected by the solution pH [38].

Saadat *et al.*, (2011) studied the optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies. Different variables affect Pb(II) removal efficiency. The effects of solution pH, adsorbent dose, initial concentration of Pb(II) ions, and temperature on metal removal efficiency were examined in a batch system [39].

From the literature, it is clear that many researchers are studying the removal of heavy metals from aqueous solutions by using various bio-adsorbent such as walnut shells, almonds shells, wheat bran, bamboo charcoal, banana peels, etc. Using biomass is eco-friendly and not hazardous as well as a low-cost effective technique. So, researchers are more focusing on the removal of lead and cadmium by agro-based waste than the ion exchange resin technique (Almasi *et al.*, 2012) [40]. Shruthi *et al.*, (2018) studied the removal of heavy metals from wastewater using walnut shells as an adsorbent by using a flame atomic absorption spectrometer [41]. Wolfova *et al.*, (2013) studied the removal of lead from an aqueous solution by the walnut shell. The important parameters such as equilibrium and kinetics were studied. Walnut shells were activated by NaOH at different concentrations of 0.01, 0.1, 1, and 2 mol/L, and the time of activation was found to be 5,15,30,45 min. This was found to be the most effective chemical treatment of bio-sorbent [42].

Based on these findings, this research has been focused on chemically modified charred and xanthated adsorbent prepared from walnut shells for the removal of lead(II) ion from aqueous solution.

CHAPTER 4

MATERIALS AND METHODS

All the experiments were carried out using xanthated walnut shells (XWS) which were prepared from the walnut shell collected from the local market in Asan, Kathmandu, Nepal in 2021 March. All the chemicals used were LA/AR grade and were used as received.

4.1 Instruments & Chemicals or Reagents Used

The instruments that have been used during the research are listed below:

1. Laboratory mill (grinder)
2. Sieve number 150 (India)
3. Weighing Balance
4. Mechanical shaker
5. Digital pH meter (Labotonics-11, India)
6. AAS (Nova 350, Analytica)
7. Double beam UV-VIS spectrophotometer (Labotonics LT-2802)
8. Hot air oven
9. Desiccator

Table 3.1: Chemical employed in the work

S.N	Name of the chemicals	Manufacturer name	%Purity
1	Potassium Hydroxide (KOH)	Loba chemie	98
2	Lead nitrate $Pb(NO_3)_2$	Fisher scientific	98
3	Sulphuric acid (H_2SO_4)	Fisher scientific	98
4	Hydrochloric acid (HCl)	Qualigens fine chemicals	97
5	Buffer Tablets of pH 4 & 7	Qualigens fine chemicals	-

4.2 Preparation of raw adsorbent material

Walnut shells were collected from the local market of Asan Kathmandu Nepal in Falgun of 2077 (March, 2021). Collected walnut shells were washed with distilled water for the complete removal of loosely held particles from the walnut shell. Washed walnut shells were then sun-dried and oven dried for 1 day for complete removal of moisture from the walnut shell. Completely dried walnut shell was ground with 6000 rpm ball mill to make powder form. The complete dry powder is labeled as raw adsorbent material.

4.3 Preparation of charred walnut shell powder

For the preparation of charred walnut shell powder, 200 g of the raw adsorbent material was taken in a bucket of 5 L capacity, and the charring process was carried out by adding 200 mL of concentrated Sulphuric acid (Fisher Scientific, Sp.gr 1.834-1.836g, % purity 98), to it and stirred thoroughly with a glass rod under fumehood until it turns completely black. While charring, a small quantity of concentrated H_2SO_4 was added at a time in installment till it turns completely black. Thus, obtained black powder of walnut shell was leftover for 24 hrs. The charred sample was washed several times with deionized water until the pH of the water obtained after washing reached neutral i.e. pH 7 then dried in a hot air oven for 24 hrs at 40 °C for complete removal of moisture from it. Thus, obtained charcoal was ground thoroughly and sieved with 150 μ m. Finally, 150 g charred sample obtained was kept in a desiccator for 1 hrs and stored in an airtight bottle.

4.4 Preparation of xanthate walnut shell

Xanthate walnut shell was prepared by taking 75 g of the charred walnut shell in a 500 mL beaker. Then 375 mL of 15 % KOH solution was added into it and magnetically stirred for 3 hrs at a speed of 200 RPM. Then, 20 mL of carbon disulfide was added into it and again shaken for 10 hrs with the aid of magnetic stirrer and left for overnight. The solution was washed with distilled water and then with double distilled water for making the sample neutral. Thus obtained charcoal was then shade dried for 2 days and oven-dried for 15 hrs at 40 °C for complete removal of moisture from the charcoal. Finally, thus obtained xanthated walnut shell (55 g XWS) was kept in a desiccator for 1 hr and stored in an airtight bottle.

4.5 Preparation of reagents

4.5.1 Preparation of 1000 ppm of lead (II) solution

For the preparation of a 1000 ppm stock solution of lead nitrate, 1.6 g of lead nitrate was dissolved in a 1000 mL volumetric flask. 1000 ppm of stock solution of the lead solution was stored in a volumetric flask and different concentrations of working solutions were prepared from it by serial dilution method.

4.5.2 Preparation of buffer solutions

Standard buffer solutions were prepared by dissolving each tablet of pH 4 and 7 separately, in distilled water making the total volume of 100 mL for each case.

4.5.3 Preparation of 15 % of potassium hydroxide (KOH) solution

15% KOH solution was prepared by dissolving 75 g of potassium hydroxide in water to make volume 500 mL.

4.5.4 Preparation of 1M sodium hydroxide (NaOH) solution

1M NaOH solution was prepared and diluted forward as per requirement.

4.5.5 Preparation of 1M hydrochloric acid (HCl) solution

250 mL of 1M HCl solution was prepared by from hydrochloric acid available at Amrit campus chemistry laboratory and the solution was diluted forward as per requirement.

4.6 Characterization of adsorbent

Walnut shells and chemically modified walnut shells were prepared for the effective removal of lead. Characterization of the chemically modified walnut shell was done for the study of the surface structure, morphology, and functional groups present in the bio-adsorbent which show the adsorption capacity of the activated charcoal. For which the following characterization tools were used.

4.6.1 Fourier- transform infrared spectroscopy

The functional group study was carried out using fourier transform infra-red radiation (FTIR, Perkin Elmer Spectrum GX, USA). The FTIR spectrum of walnut shell dust, XWS before and after adsorption of lead ions were analyzed at the Amrit campus in

Thamel Kathmandu Nepal. In FTIR spectroscopy, IR radiation was passed through the sample, some of the radiation was absorbed by the sample and some were transmitted through the sample. The resulting spectrum represented the molecular adsorption and transmission, creating the molecular fingerprint of the sample. The effects of the presence of the surface functional group on the adsorption of lead were analyzed by observing the shifting of the FTIR peaks after the adsorption experiment.

4.6.2 Field Emission Scanning electron microscopy (FE-SEM)

The morphology of as-prepared activated carbon was studied using field emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra-40, VP Germany) at an accelerating voltage of 5.0 kV. Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column, these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relate to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed into a video scan-image that

4.7 Adsorption study

Adsorption study was performed using the working solution of the lead nitrate, and XWS as an adsorbent. The working solutions of the required concentrations were prepared using the stock lead(II) solution of 1000 ppm. 25 mg of the adsorbent and 25 mL of the lead solution were separately mixed in a reagent bottle and shaken for 3 hrs on a mechanical shaker for complete adsorption. The solution was filtered using Whatman filter paper to obtain pure liquid without the presence of the adsorbent. The absorbance of the filtrate before and after adsorption was measured using AAS and the adsorption capacity of the different adsorbents was investigated.

4.7.1 Effect of pH

The removal of heavy metal ions from aqueous solution using adsorbent depends upon the pH of the solution under study. During the study of the effect of contact time, effect of initial concentration, and adsorbent dose, optimum pH of the aqueous solution should be taken. A batch adsorption test is used for the removal of lead by

using CWS and XWS. Initial pH of the solution was maintained by using hydrochloric acid and sodium hydroxide solution. In this study, 25 mL of the lead nitrate solutions of 25 ppm concentration was taken separately in different reagent bottles with pH ranging from 1 to 9. Then 25 mg of the adsorbent (CWS and XWS) was poured into those reagent bottles containing solution of different pH (1 to 9). Each of the reagent bottles was then agitated in mechanical shakers at room temperature with 200 rpm for about 5 hrs. to attain equilibrium. The solutions after agitation were kept at a standing position for an hour and then they were filtered using the filter paper. The absorbance of the filtrate was taken using AAS. pH at which the absorbance of the metals was maximum for CWS and XWS is the optimum pH of the solution. The pH affects the solubility of the metal ion ionization state of functional groups, such as carbonyl, phenols, hydroxides, amino groups, and hydrocarbons of the cell wall. Optimum pH for XWS can be the same or different.

4.7.2 Kinetic studies of adsorption of lead

Time consumed by the adsorbents for the maximum removal of the lead using CWS and XWS was optimized through the effect of the contact time at room temperature. For this study, 25 mL of the solution of the metal (i.e. lead) having 25 ppm concentration with optimum pH was taken in a reagent bottle. 25 mg of the adsorbent was added to the separate bottles and agitated with the help of a mechanical shaker at 200 rpm speed. Adsorption data were taken in a regular interval of time at 30, 60, 120, 150, 180, 210 min. and so on. Then the sample was collected, filtered and then analyzed. The absorbance of the heavy metals before and after adsorption was determined using AAS till the adsorption amount of the metals reached constant value i.e. no more adsorbate gets adsorbed after that time. By using absorbance, concentration was determined. To determine the adsorption kinetics of the heavy metal, kinetic parameters for the adsorption process were analyzed for contact time ranging from 30 min till complete adsorption time. By calculating the % absorbance of the lead at the respective time for CWS and XWS data obtained were analyzed using Lagergren's pseudo-first-order and pseudo-second-order kinetic models. The removal kinetics of the lead was analyzed by drawing the data obtained after desired time.

4.8.3 Adsorption isotherm study

The adsorption isotherm curve relates with the amount of adsorbed per unit mass of the adsorbent to the amount of the un-adsorbate adsorbate remaining at the solution at equilibrium time. For this, 25 mL of optimum pH adjusted lead metal solution of different initial concentrations were taken in a separate bottle to which 25 mg of adsorbent was added and made airtight. The solution was agitated for 3 hours in a mechanical shaker at 200 rpm and kept 24 hours. The agitated sample was filtered and adsorption was tested in Atomic absorption spectroscopy (AAS) and adsorptions at different initial concentrations were analyzed before and after adsorption. The adsorption isotherm model was studied through the data obtained from the study of the effect of the initial concentration of metal.

CHAPTER 5

RESULT AND DISCUSSIONS

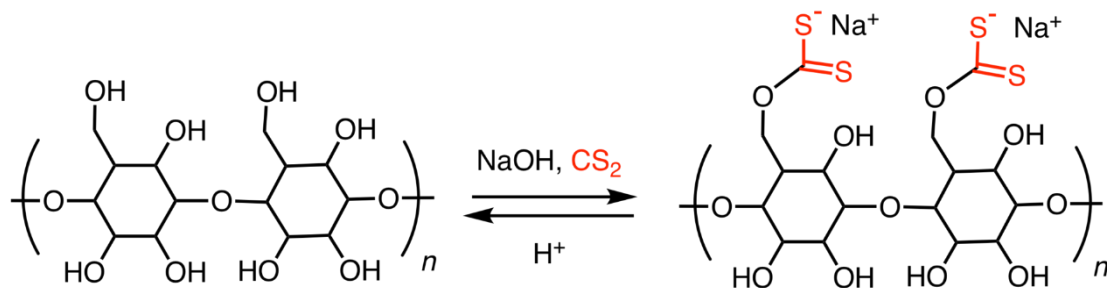
5.1 Synthesis of adsorbent materials

The ground and dried walnut shell was obtained as brown powder which is raw adsorbent material and is named as raw walnut powder hereafter (RWP). Upon treating the RWP with concentrated sulphuric acid, a black powder was obtained which was washed several times to obtain neutral charred material which is named as charred walnut (CW) hereafter. Concentrated sulphuric acid has capacity of dehydration from hydrocarbon leaving behind carbon only. The hydrates part (i.e., water molecules) of carbons get adsorbed by conc. Sulphuric acid by its dehydrating action.

Xanthation is the process of treating alcoholic functionalities with alkali (e.g., KOH) followed by carbondisulphide which result into the formation of ester of dithiocarbonate ($\text{RCOS}_2^- \text{M}^+$), where R is alkyl group and M is metal ion. Simply, xanthate is the salt of any xanthic acid ($-\text{COS}_2\text{H}$). The CW was treated with 15 % KOH followed by carbondisulphide for xanthation which is termed as xanthated walnut powder (XWP) hereafter. Here, potassium hydroxide converts the alcoholic group into alkoxide which serves as nucleophile and harbours the electrophilic carbon center of CS_2 .



Herein, if some remnant of cellulose are there even after charring gets reacted with carbondisulphide in presence of strong alkali such as KOH or NaOH to give potassium/sodium cellulose xanthate. As-introduced sulphur atom is expected to chelate metal ions during the process of heavy metal ions removal.



5.1.1 Physicochemical characterization

a. FESEM study

The FESEM image of raw walnut powder (RWP), charred walnut (CW) and xanthated walnut powder (XWP) at different magnification are displayed as in the figure.

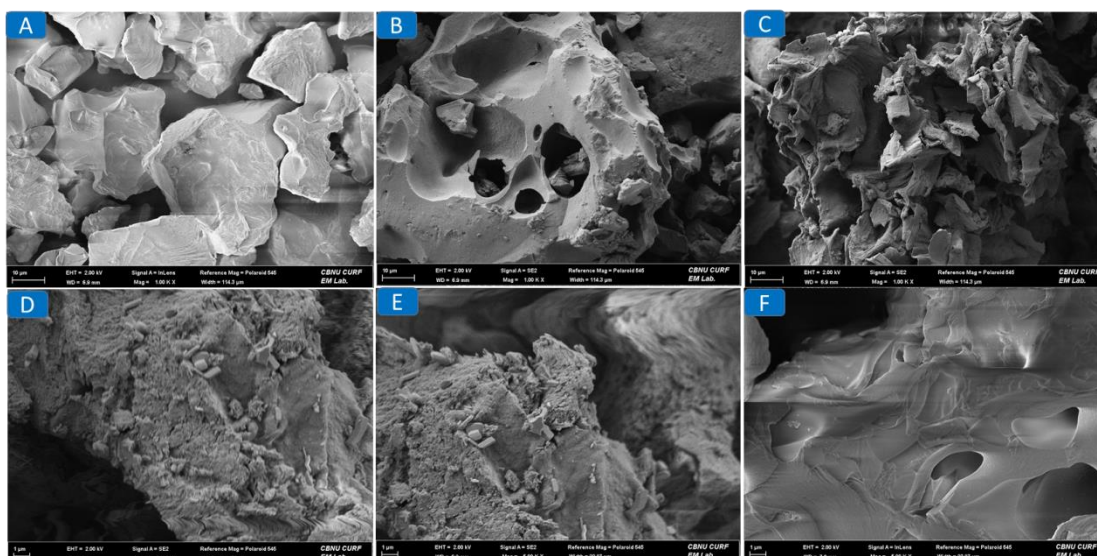


Figure 1: FESEM image of raw walnut powder (A and D), charred walnut (B and E) and xanthated walnut powder (C and F) at a magnification of 1KX (scale 1 μm) and 5 KX (scale 10 μm).

The image showed that charring of the raw walnut shell developed the porosity and xanthation process introduces carbondisulphide where Sulphur can chelate metal ions and hence assists the removal of metal ions. The xanthation was carried out by treating 15 % KOH solution followed by CS₂. The EDX image showed the presence of carbon, Sulphur and potassium in the mapping. Additionally, the presence of oxygen could be due to the presence of oxides forms. The elemental mapping explicitly showed the successful xanthation process.

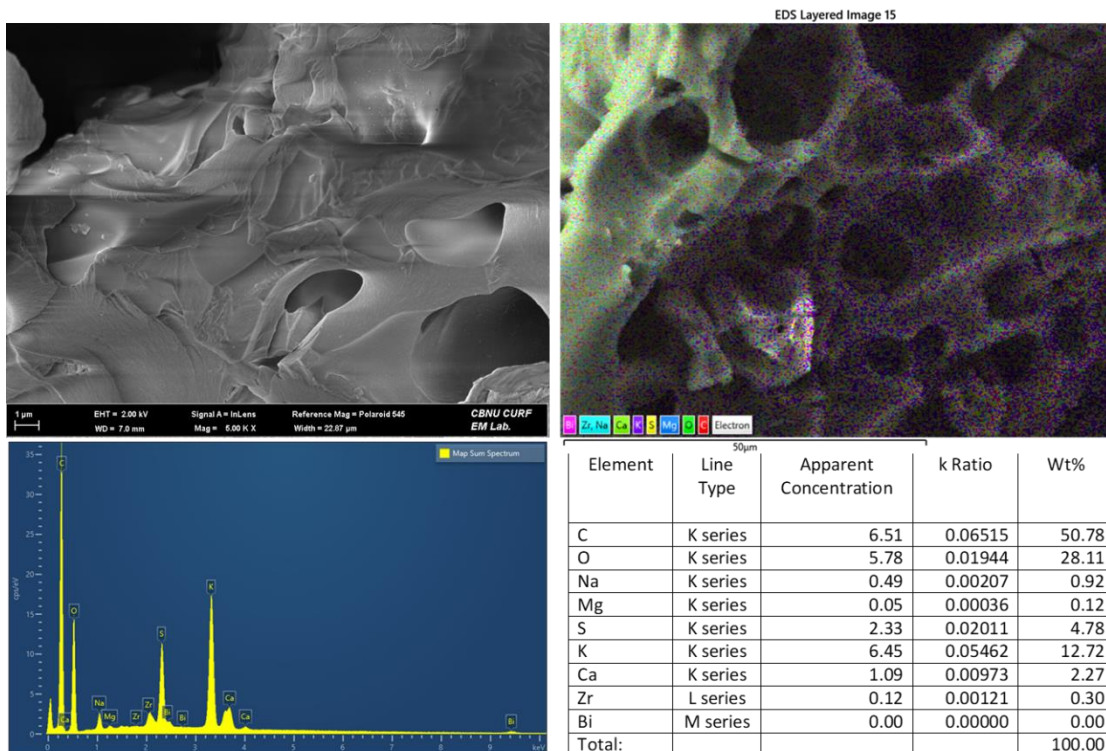


Figure 2: EDX spectra of as-synthesized xanthated carbon with elemental mapping.

b. FTIR study

Figure 3 shows the FTIR spectra of different stage of walnut powder. The IR absorption peak at around 3200–3600 could be associated with the –OH stretching of phenolic or carboxylic functionality or of adsorbed water group associated with as-synthesized carbon. The peak at 14605 cm^{-1} corresponds to the aromatic C=C vibrations, symmetric stretching of –COO group and hydrogen bonded carbonyl group. The result shows that there is a slight shifting of the peak upon xanthation. Broad peak observed around 1000–1300 cm^{-1} corresponds to the oxidized carbon such as C-O- stretching, or S=O stretching. These functionalities could arise as a result of xanthation process using KOH in presence of CS_2 . These evidences supports the successful xantahtion process in the synthesized walnut powder. ...

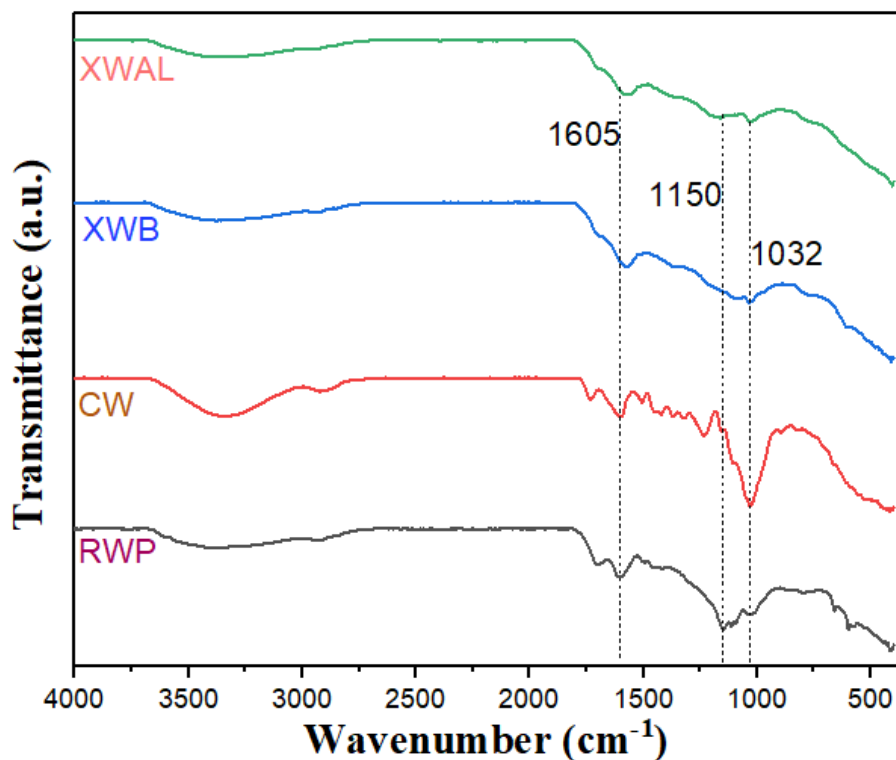


Figure 3: FTIR spectra of as-synthesized raw walnut powder (RWP), charred walnut (CW), xanthated walnut before adsorption (XWB) and xanthated walnut after lead adsorption (XWAL).

c. XRD study

[Figure 4 shows the x-ray diffraction pattern of as-synthesized activated carbon materials. The broad peak of ACs extending from 15–30 indicates the amorphous nature of carbon. Absence of sharp peak at 26° indicates the absence of degree of graphitization. The xanthated activated carbon after lead adsorption shows a sharp peak at 22° which indicates the adsorption of Pb\(II\) from the solution. This gives an evidence of adsorption of Pb\(II\) by as-synthesized activated carbon. The 2 theta angle lying between 20–25° could be associated with adsorbed lead in graph \(c\).](#)

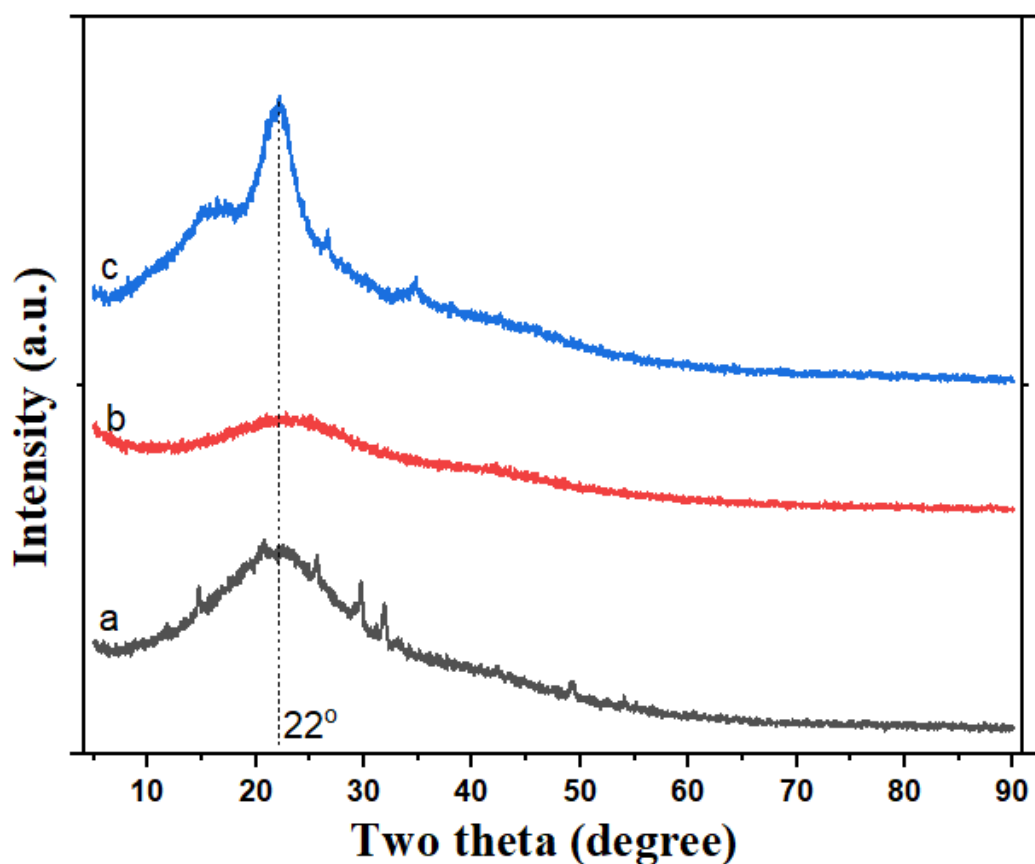


Figure 4: XRD spectra of as-synthesized (a) raw walnut powder (RWP), (b) Charred walnut shell and (c) xanthated walnut after lead absorption (XWAL).

5.2 Calibration Curve for Pb(II) Analysis

The calibration curve for the determination of Pb(II) ion has been established using lead nitrate solution of concentration 0.25, 0.5, 1, 2, and 4 ppm as shown in figure 3. The calibration curve helps us to determine a directly measurable range by the standard addition and dilution method.

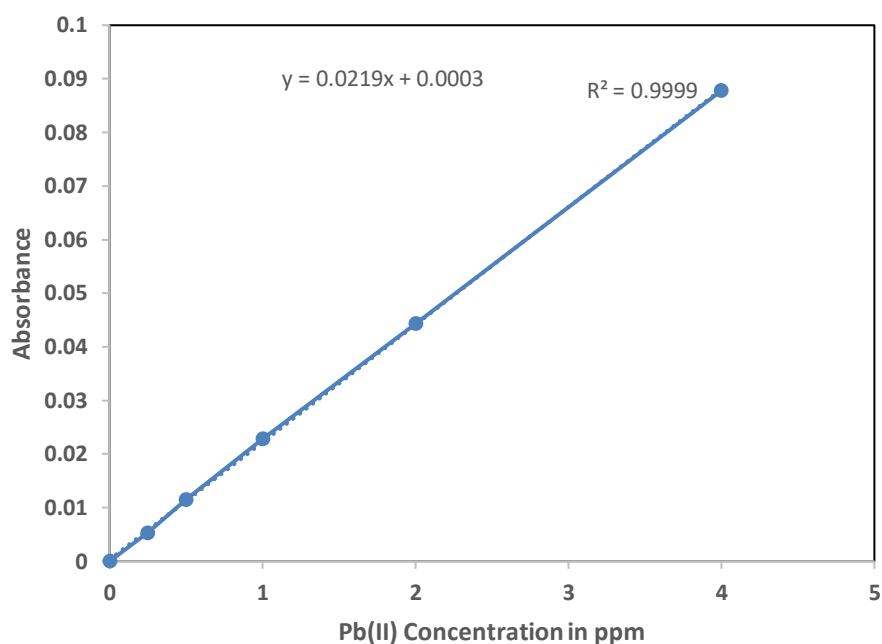


Figure 7: Absorbance versus concentration of Pb(II) in ppm

5.3 Adsorption study

Adsorption study was performed with respect to the effect of pH, effect of contact time, and effect of initial concentration. Percentage removal increased with the initial concentration and increased with an increase in contact time of modified Walnut shell. In the case of pH, percentage adsorption increased from pH 1 to till pH 4 and then gets decreased. Percentage adsorption of chemically modified XWS was found more than that of CWS because of more adsorption sites present in chemically modified activated XWS than that of CWS. Thus XWS could be employed as the best alternative adsorbent than commercial activated carbon.

5.3.1. Effect of pH

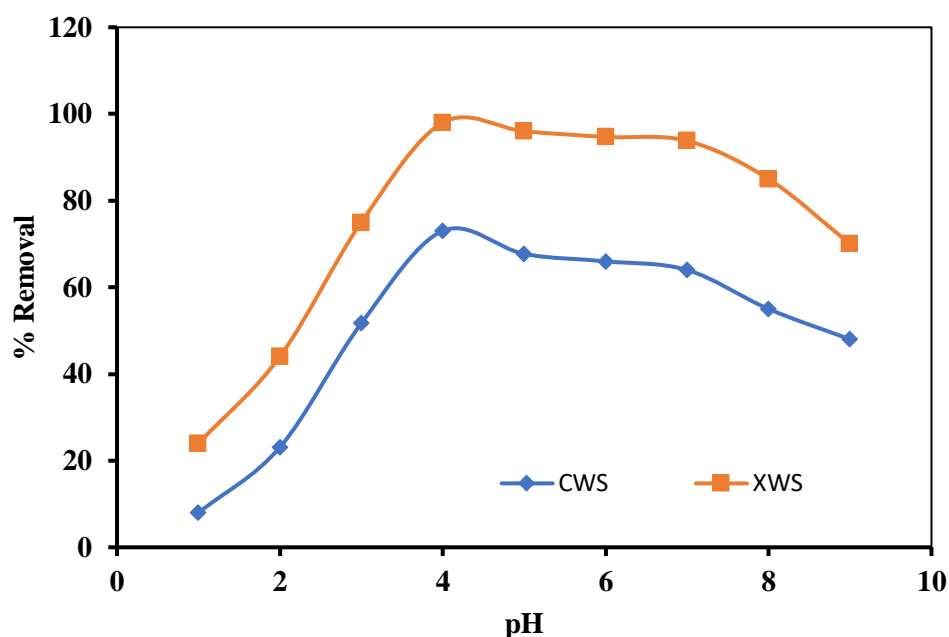


Figure 8: Effect of pH on the adsorption of Pb(II) by using CWS and XWS

The pH of the solution is the most important parameter which influences the metal ion speciation and surface properties of adsorbent and hence control the adsorption of ionic species. In this section, the influence of pH on the adsorption process with their adsorption efficiency has been analyzed at different pH. Figure 8. shows the effect of pH on adsorption of lead(II) by CWS and XWS. For this study, 25 ppm of the metal solution was taken and required pH (1 to 9 in each bottle) was maintained using a pH meter at room temperature. Then 25 mg of the CWS, and XWB was taken in a reagent bottle along within pH maintained metal solution. Adsorption study for effect of pH by bio adsorbent i.e. CWS and XWS was done separately in reagent bottle from pH 1 to pH 9. From the pH studies, it was seen that the optimum pH for the adsorption of metal ions for both CWS and XWS was found to be pH 4 i.e. maximum removal of lead ion solution was found at pH 4. This result is in quite agreement with that of Jeyakumar et al., (Jeyakumar et al., 2014). Below and above the pH 4, the adsorption of lead by the activated carbon was low. This could be associated with the surface charge of activated carbon which is greatly influenced by pH of the media. The % removal of the lead metal ion by CWS increased from 7.96% at pH 1 to 73.2% at pH 4 then again decreased up to 48 % at pH 9 whereas for XWS % removal of lead ion solution increased from 24% at pH 1 to 98% at pH 4 and then again decreased up to

70% at pH 9.

From the pH studies, it is seen that the optimum pH for XWS and CWS was found to be 4.0. It can be seen from fig 4. that the maximum percentage removal of the lead metal ion was found to be 73.2% and 98% for CWS and XWS, respectively. The metal removing ability of the XWS was found more efficient than that of the CWS probably due to the addition of the chelating group i.e. S-atom of the sulfur group which enhances the ability of the activated carbon more metal ion on the XWS. Thus, it can be concluded that the optimum pH for adsorption of lead ions by CWS and XWS is 4.0.

5.3.2. Effect of Contact Time

The contact time is another important parameter for performing the batch adsorption experiment. In this section, the amount of adsorbate uptake by both adsorbents at different time intervals has been investigated which is shown in the plot of q_t versus time in figure 3. The effect of contact time for the adsorptive removal of lead (II) ions was studied in the range of 0–250 min. The experiment was set using 25 mL solution of lead (II) of 25 ppm at pH 4 for the synthesized XWS and CWS with agitation speed of 200 rpm for 5 h at room temperature.

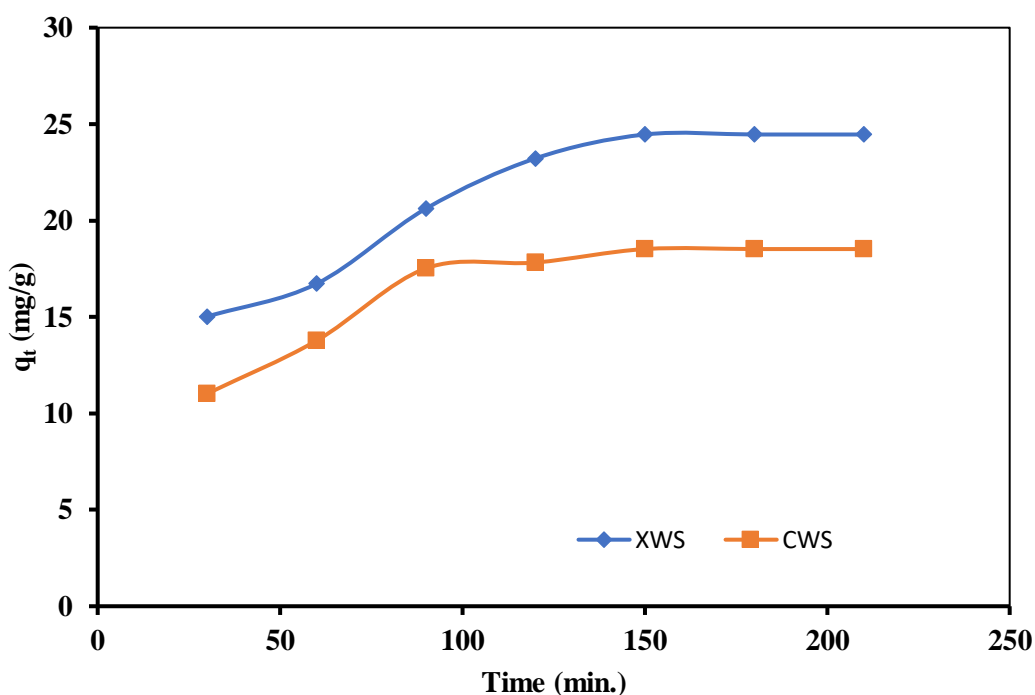


Figure 9: Effect of contact time on the adsorption of Pb(II) by using CWS and XWS.

Figure 9 showed that the equilibrium contact time for the adsorption of Pb(II) by adsorbent CWS and XWS reached within 150 minutes at pH 4 with adsorbate uptake of 18.92 mg/g and 24.46 mg/g, respectively. The adsorption of lead was initially increased with the increase of the contact time up to a certain time and then remains constant. The increase in adsorption at the initial time is due to the availability of a large surface area of adsorbents for the adsorption of Pb(II). After the equilibrium has reached, the adsorption rate slows down and eventually becomes constant due to the difficulty of occupying the remaining vacant surface.

The above discussion concludes that the chemically modified XWS adsorbent has more metal uptake efficacy than CWS at this optimum time.

5.3.3. Effect of Initial Concentration

The effect of initial concentrations on adsorption of Pb(II) was studied by varying the concentration of an aqueous solution from 10 mg/L to 800 mg/L with the chemically modified walnut shell i.e. CWS and XWS at optimum pH 4. The plot of C_i vs. q_e for the adsorption of Pb(II) as shown below.

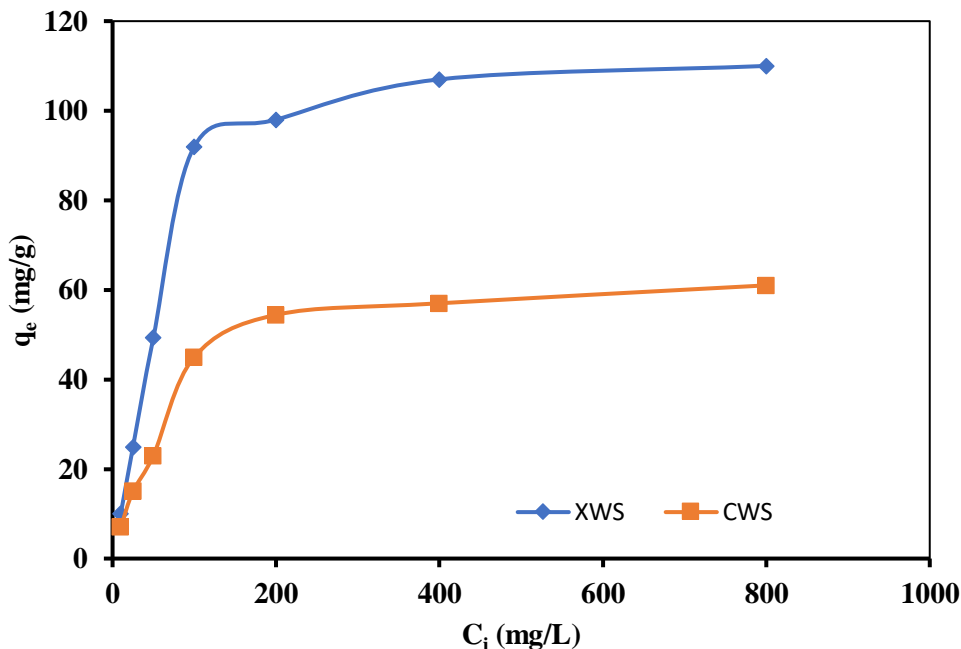


Figure 10: Effect of initial concentration on the adsorption of Pb(II) by CWS and XWS.

The experimental data showed that the maximum adsorption capacity of CWS and XWS was 61 mg/g and 110 mg/g, respectively which are shown in fig 10. It is found

that the adsorption capacity of XWS is better than that of the CWS. This curve indicates that the sorption capacity will increase with the increase in the initial concentration gradient. At lower initial concentration, sufficient sorption sites are available for the sorption of the metal ions therefore, at higher initial concentration, the numbers of metal ions are relatively higher than adsorption sites; hence the removal percentage depends on the initial concentration. This occurs due to the increase in the rate at which Pb(II) ions pass from the bulk solution to the particle surface along with the increase in the concentration of the solution that would result in the higher adsorption.

5.4. Adsorption Isotherm Studies

The adsorption isotherms help to determine the design of the adsorption mechanism between adsorbate and adsorbent systems. To evaluate the best-fit isotherm model for Pb(II) adsorption, the experimental data of Pb(II) adsorption onto CWS and XWS were analyzed using the well-known Langmuir and Freundlich isotherm equation. Linear plots were obtained in both models which are illustrated in figure 7.

In figure 7, the plot of C_e/q_e vs C_e showed the straight line that indicates the experimental data of Langmuir linearized isotherm for Pb(II) onto adsorbents i.e. CWS and XWS. Here, the maximum adsorption capacity (q_m) for CWS and XWS were found to be 61.012 mg/g and 109.90 mg/g, respectively. Similarly R_L values from the Langmuir isotherm modes were found to be 0.99 and 0.99 for CWS and XWS. These values were found to be in the range of $0 < R_L < 1$ which indicates that the process is favorable and adsorption data fit well in the Langmuir adsorption isotherm.

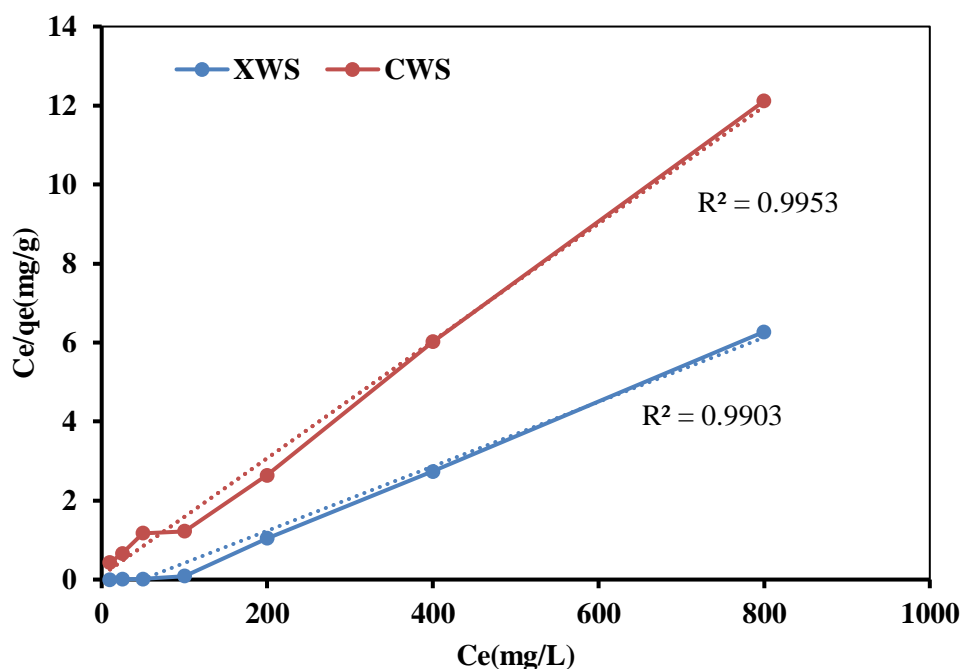


Figure 11: Langmuir Adsorption isotherm for adsorption of Pb(II) onto CWS and XWS

Table 3: Langmuir parameter for the adsorption of Pb(II) onto CWS and XWS

Metal	q_e (mg/g)	R^2
Pb(II) onto CWS	61.01	0.99
Pb(II) onto XWS	109.9	0.99

The plot of q_e vs c_e showed the straight line that indicates the experimental data of Freundlich linearized isotherm and provides the value of $1/n$ as 0.89 and 0.84 for CWS and XWS, respectively. Here the value of $1/n$ for the adsorbent lies in between 0 and 1, which indicated that the Freundlich isotherm also followed by the resulting data. But the experimental data presented in figure 11 and 12 revealed that the Langmuir isotherm model for both adsorbents showed a better fit than the Freundlich isotherm.

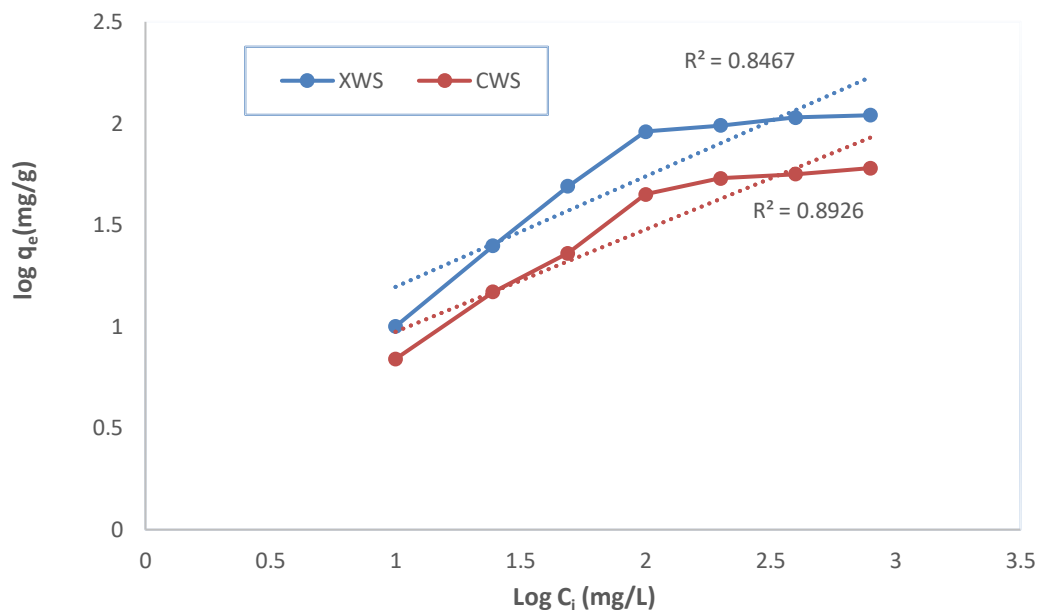


Figure 12 : Freundlich adsorption isotherm for adsorption of Pb(II) onto CWS and XWS

Table 4: Freundlich parameter for the adsorption of Pb(II) onto CWS and XWS

Metal	q _e (mg/g)	R ²
Pb(II) onto CWS	61.01	0.84
Pb(II) onto XWS	109.9	0.89

5.5. Batch Kinetics Studies

The experimental kinetic data for the adsorption of Pb(II) onto CWS and XWS were studied by using different kinetic models such as pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-second order plot of $\frac{t}{q_t}$ vs. time gave the perfect straight line for the adsorption of Pb(II) metal onto CWS and XWS simultaneously indicating that the adsorption reaction can be followed from the pseudo order kinetic model. In this study, the R² was found to be 0.994 and 0.991 and equilibrium concentration q_e for the adsorbents were found to be 18.25 mg/g and 24.44 mg/g for CWS and XWS, respectively.

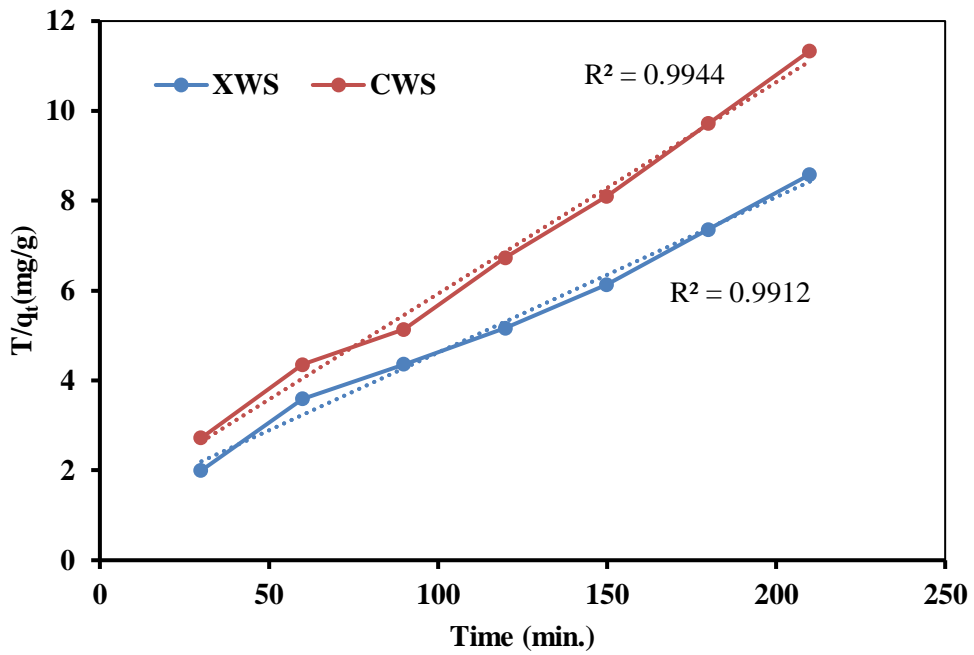


Figure 13: Pseudo second order kinetics model for adsorption of Pb(II) onto CWS and XWS

In figure 13, the experimental kinetics data for adsorption of Pb(II) was studied, and the plot of $\log(q_e - q_t)$ vs time showed a downward straight line which indicates the pseudo-first-order reaction with respective slope, intercepts, and correlation coefficient R^2 . In this study, the R^2 was found to be 0.93 and 0.91 onto CWS and XWS, respectively.

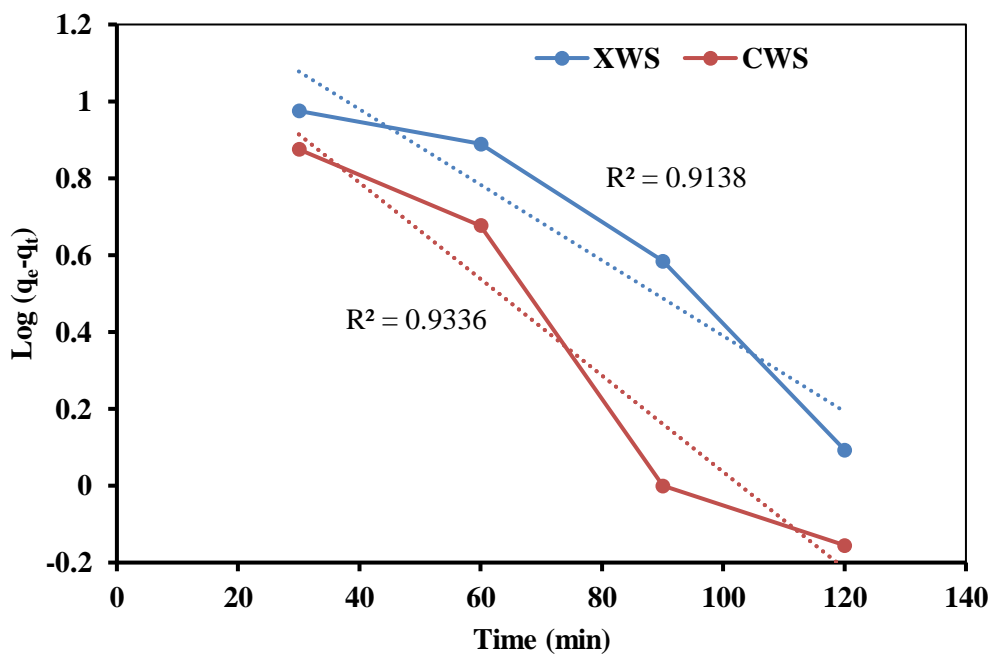


Figure 14: Pseudo-first-order kinetics model for adsorption of Pb(II) onto CWS and XWS.

So, by the investigation of the kinetic data for the adsorption of lead from lead nitrate, a straight line with the best fitting and high correlation coefficient value was observed in the case of pseudo-second-order than first order. The experimental data followed pseudo-second-order for both adsorbents.

Table 5: Pseudo first-order kinetics model for adsorption of Pb(II) onto CWS and XWS

Adsorbent	Pseudo-first order			Pseudo-second order		
	Slope	$q_e(\text{mg/g})$	R^2	slope	$q_e(\text{mg/g})$	R^2
CWS	-0.0098	18.92	0.933	0.047	18.92	0.99
XWS	-0.012	24.44	0.91	0.034	24.44	0.99

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1. Conclusion

In the present work, walnut shells were successfully charred and xanthated. Different physicochemical properties of the easily available waste biomass 'Walnut shells' and its modified forms were investigated. Its efficiency for removal of Pb(II) was determined by varying different parameters. The functional group present in bio adsorbent was characterized by FTIR analysis. The adsorption of lead was found to be strongly dependent upon the pH of the solution and the optimum pH value for the adsorption was determined to be 4 for both CWS (with 73% adsorption) and XWS (with 98% adsorption). At the optimum pH value of 4, CWS lead to 73% removal of Pb(II) from the aqueous solution whereas XWS was found to be tremendously effective with 98% removal. Hence, it could be concluded that the XWS adsorbent was by far better at removal of the Pb(II) from aqueous solution than CWS adsorbent.

The equilibrium time for adsorption of Pb(II) onto both CWS and XWS was found to be 150 min. The maximum adsorption capacity of CWS and XWS was found to be 61.03 mg/g and 109.9 mg/g respectively. The adsorption isotherm study revealed that the Langmuir adsorption isotherm can best explain the adsorption of Pb(II) onto both CWS and XWS. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic models. It was found that the obtained data were best fitted for the pseudo-second-order kinetic model. This research work concludes that the walnut shell can be used as a potential bio-adsorbent for the removal of Pb(II) from an aqueous solution.

6.2 Limitation of the Study

Every experiment in this research was performed carefully and wisely as far as possible to minimize errors and limitations. However, the following limitation of the study is subjected.

- a. Chemicals were not subjected to further purification before the experiment.
- b. Characterization like XPS and TEM were not performed due to time and budgeting constraints.
- c. The experiment in column mode was not performed.

6.3 Suggestion for Further Study

Application of walnut shell to remove other heavy metal ions such as Cd(II), Cr(II), Ni(II), Cu(II), and Zn(II) ions, as well as dyes present in commercial industries, wastewater such as Methylene Blue, Congo Red, and Reactive Yellow can be performed. An experiment in column mode can be carried out to study the effect of the further parameter.

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