









Removal of Pb(II) from aqueous solution using xanthate modified waste walnut shells

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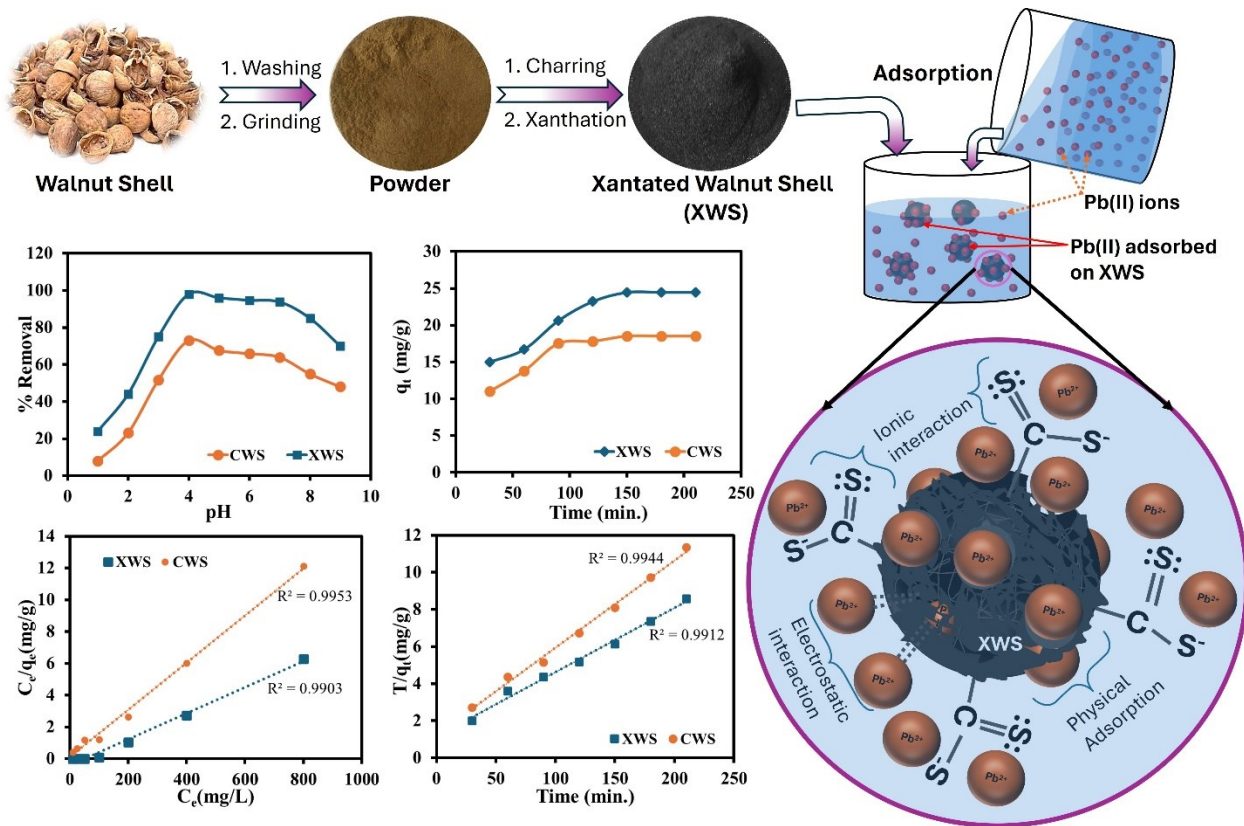
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Abstract

A vast number of biomass-based materials are getting increasing attention for heavy metal removal and recovery due to their good performance, low cost, large availability, and environmental friendliness. This study primarily aims to fabricate a cost-effective, potent adsorbent derived from walnut shells through chemical modification, targeting the removal of Pb(II) ions from water. The experimentation involves the preparation of adsorbents from charred walnut shell (CWS) and xanthated walnut shell (XWS), followed by batch trials to eradicate Pb(II) from water. Parameters for instance pH, concentration of Pb(II), adsorbent quantity, and contact duration were examined using both CWS and XWS adsorbents. For characterization purposes, FTIR, XRD, and FE-SEM analyses were employed. Optimal conditions were identified at pH 4 and duration of contact 150 minutes for both adsorbents. Equilibrium sorption data adhered best to the Langmuir isotherm model, with maximum adsorption capacities of 61 mg/g for CWS and 109.9 mg/g for XWS. Kinetic modeling showed the well-fitting of pseudo-second order kinetic. These findings suggest that XWS presents a promising, eco-friendly alternative bioadsorbent intended for the elimination of lead (II) from water.

Keywords: Walnut shells, Adsorbent, Xanthation, Bio-sorbents, Lead (II) removal

Graphical abstract:



1.0 Introduction

Though defined differently, heavy metals are commonly understood to be metallic elements with relatively high density and atomic weight. Typically, substantial heavy metals have a density of around 5 g/cm³ or higher and atomic weight greater than 20 (Khalef et al., 2022). Some common naturally available heavy metals in the earth crust includes lead (Pb), copper (Cu), silver (Ag), zinc (Zn), mercury (Hg), arsenic (As), iron (Fe), cadmium (Cd), etc. (Homagai et al., 2023). Though the term “heavy metal” literally refers to the elements with high density, its understanding has been evolved to primarily emphasize their toxicity and ecotoxicity rather than physical properties (Duffus, 2002). Even a low concentration (in ppb level) of such metal ions in drinking water can cause a serious threat to the health. In this context, World Health Organization (WHO) has provided guidelines and recommendations for the maximum permissible level of such heavy metals in drinking water to ensure its safety for human consumption. The upper permissible levels of heavy metal ions in drinking water as set by WHO are very low; cadmium (3 ppb), mercury (6 ppb), arsenic (10 ppb), lead (10 ppb), chromium (50 ppb) and so on (WHO, 2022).

Lead, a representative heavy metal, is known for its toxicity and its ability to infiltrate the water systems through natural and anthropogenic pathways. Though lead is present in trace level in the earth crust, the anthropogenic activities like mining, burning fossils fuels, using dyes and many industrial products can lead to the exposure (Vareda et al., 2019). Lead is widely used across numerous industries, including the production of batteries, paints, firearms and as an additive in fuels. Industrial activities along with the combustion of fossil fuels, mining and vehicular emission facilitate release of the lead into the environment which on ingestion, inhalation, or dermal absorption in the body of living being induce the medical condition known as "plumbism" or "saturnism" which possesses severe health risks, especially for children (Montes-Santiago, 2013). The detrimental health effect includes cognitive impairment, diminished

intelligence quotient (IQ), anemia, and organ toxicity (Yi et al., 2015). Neurological disorders, organ failure, and hematological anomalies are familiar penalties of prominent levels of lead in the biological systems. Its tendency to bioaccumulate presents ongoing risk to organisms and disrupts ecological integrity, as it resists biodegradation and detoxification processes (Khatun et al., 2022).

Lead ions (Pb^{2+} & Pb^{4+}) are characterized by their propensity to bio-accumulate and their resistance to degradation into non-toxic end products (Collin et al., 2022). Population predominantly depending on the groundwater resources for both agricultural and drinking water greatly suffers from the heavy metal contamination, particularly lead and its detrimental effects on health. Therefore, it is crucial to remove lead (Pb) from drinking water to protect human health and the environment.

Consequently, the recovery and removal of lead (Pb) from wastewater have thus emerged as pivotal point of research in water treatment. Commonly employed methodologies for lead abatement encompass oxidation-reduction processes, precipitation, ion exchange (Wu, et al., 2021), coagulation-flocculation, bioremediation (Rigoletto et al., 2020), membrane-based separations (Hajdu et al., 2012), electrochemical method (Liu et al., 2013), and adsorption (Cruz et al., 2020). All these techniques have challenges either in terms of economy or in terms of efficacy. In addition, it is necessary to remove toxic contaminants by ensuring environmental safety. Among the different methods, adsorption stands out in terms of its efficiency, cost-effectiveness, and reversibility.

Agricultural waste materials such as date stone, walnut shell, corn corb, pistachio shells, cassava peel, olive cake, cow dung, orange peel, nutshell, sawdust, etc. have demonstrated exceptional adsorptive capacity for heavy metals (Ibrahim et al., 2022; Nejadshafiee & Islami, 2020; Saraswat et al., 2020; Tejada-Tovar et al., 2021). These materials inherently contain cellulose, hemicellulose, and lignin which exhibit a natural affinity towards heavy metal ions. Chemically treating these materials to produce activated carbon with abundant unsaturated binding sites can improve their effectiveness as bioadsorbents. Being a cost-effective and efficient approach, activated carbon is employed as bio-sorbents. In comparison to other treatment options, biosorption provides a number of benefits, including low sludge production, cost-effectiveness, efficiency, and the potential for metal recovery (Priyadarshane & Das, 2021). The equilibrium sorption capacity can be described by adsorption isotherms like Langmuir and Freundlich, which are often employed in adsorption process modeling (Das et al., 2024). Both batch adsorption and column adsorption techniques can be used to conduct adsorption investigations (Khalil et al., 2023). Raikar et al. (2015) studied the lead (II) removal form aqueous solution by utilizing rice husk in natural and activated state. The percentage amputation of Pb(II) were found to be 93.36, 94.80, 96.72 and 99.35 % with adsorbents rice husk, rice husk ash, phosphoric acid treated rice husk and acetic acid treated rice husk, respectively with an adsorbent dose of 4 g. The equilibrium relationship between concentration of adsorbate held on the surface of an adsorbent and concentration of adsorbate was analyzed in terms of Freundlich adsorption isotherm with pseudo-second-order adsorption kinetics (Raikar et al., 2015). Homagai et al. investigated the removal of heavy metals from wastewater using charred xanthated sugarcane bagasse (CXSB), finding that adsorption kinetics following a pseudo-second order model. Langmuir isotherm delivered an excellent adequate for the symmetry sorption statistics obtained from elemental analysis (Homagai et al., 2010). In a study conducted by Yang et al., the ferric-activated biological sludge (SBA) indicated a well-built pore configuration and superior adsorption capability for Pb(II), having a capacity of 42.96 mg g⁻¹ (Yang et al., 2019). However, finding an adsorbent with high adsorption capacity is crucial for environmental remediation. Though,

walnut shell has been used in the preparation of adsorbent, there is plenty of space for increasing its efficacy for the removal of heavy metal ions. One of the approaches could be to introduce the sulphur containing functional group or xanthate functionalization (Wang et al., 2021). It is hypothesized that introduction of sulphur into the carbonaceous materials can provide the sites for good capturing of heavy metal ions according to hard and soft acid-base principle.

In these lacunae, a novel, affordable, and efficient adsorbent was prepared utilizing walnut shell waste. *Juglans regia*, commonly known as walnut (Okhar), is an abundantly available biomass with considerable potential for the sequestration of heavy metal ions. The walnut shell is a bio-waste after the consumption of the fruit part. Adsorbent material has been prepared by charring walnut shell followed by xanthation with carbon disulphide. Finally, this material was used for the sequestration of Pb(II) ions from water.

2.0 Experimental Procedures

2.1. Materials and Reagents

Sulfuric acid (Fisher Scientific, Sp.gr. 1.835 g/mL, 98 % purity), potassium hydroxide (KOH Mol. wt. 56.11, Qualigens), carbon disulfide (CS₂, Thermo Scientific Chemicals, 99.9 %), lead nitrate (Aldrich, 99.99 %, Mol wt. 331.21) were used for this experiment as received without further purification.

2.2. Synthesis of Walnut Shell Derived Adsorbent

Walnut shells were procured from the local market in Asan, Kathmandu, Nepal. The acquired materials were subjected to a rigorous cleaning process followed by sun-drying for a day to eliminate particulate contaminants and moisture. Subsequent to drying, the shells were pulverized into a fine powder using herbal medicine disintegrator (Model: FW177), designated as the raw walnut powder (RWP).

The synthesis of charred walnut shell powder entailed treatment of RWP (200 g) with 200 mL of concentrated sulfuric acid (H₂SO₄). The mixture was subjected to a continuous agitation until homogeneously black suspension was obtained. Incrementally, sulphuric acid was added repeatedly. The resulted black suspension was allowed to stand for 24 h followed by subjecting to subsequent washing with distilled water and deionized water until a neutral pH was attained. It was then dried in a hot air oven for 4 h at 70 °C followed by vacuum drying for 4 h to ensure complete dehydration. The dried charcoal was then mechanically ground in agate mortar pestle and sieved using a 150 µm mesh. The final charred sample was subsequently placed in a desiccator for 2 h to remove the moisture and it was stored in an airtight container. For the xanthation process, initially, 75 g of charred walnut shell was treated with 375 mL of 15 % KOH. The mixture was then homogenized using magnetic stirrer for 3 hours. Then, 20 mL carbon disulfide (CS₂) was introduced to the mixture followed by thorough agitation for 10 h and subsequently left to stand overnight. The mixture was then thoroughly washed using distilled and double distilled water to attain the neutralization. It was then allowed to shade dry for 48 hours and consequently placed in hot-air-oven for 15 hours at 50 °C in order to remove residual moisture. Then it was vacuum dried for 4 h at 70 °C. With the acquisition of 55 g of the xanthated walnut shell (XWS) the process was terminated and it was ready for further characterization.

2.3 Characterization of Adsorbent

The physicochemical characterization of the synthesized charred walnut shell powder and

xanthated walnut shell were conducted using Fourier-transform infrared spectroscopy (FTIR, Perkin Elmer, 580B infrared spectrometer, USA) and Field Emission Scanning Electron Microscopy (FE-SEM, Carl Zeiss, Germany). The crystallinity of the material was studied from X-ray powder diffraction (XRD) method (Rigaku X Ray Diffractometer, Japan), at wavelength 1.54 Å within the range of 5 to 90°. These analytical techniques were employed to elucidate the surface morphology, structure, and presence of functional groups present in the bio-adsorbent.

2.4 Adsorption Study

Lead nitrate solution was utilized for studying the Pb(II) adsorption efficacy of XWS adsorbent. A stock solution of 1000 part per million (ppm) lead (II) solution was prepared and was diluted to the required concentration using the stock solution. 25 mg of the adsorbent was put into 25 mL of the lead solution in a reagent bottle and shaken for 3 hours on a mechanical shaker at 200 rotation per minute (RPM) to facilitate complete adsorption. Whatman filter paper was used to separate the adsorbent from the solution after agitation. Afterwards, Atomic Absorption Spectroscopy (AAS) was used to quantify the adsorptive performance of bio-adsorbents by measuring pre- and post- adsorption. The percentage of metal-ion adsorption (A%) is calculated using;

$$A\% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The equilibrium up take adsorption capacity in mg/g was studied using the following relation;

$$q = \frac{C_i - C_e}{m} \times V \quad , \quad (2)$$

where 'c_i' is the preliminary concentration, 'c_e' is concentration at equilibrium state, 'V' is the volume of adsorbate in milliliter and 'm' is the mass in milligram.

The optimal interaction phase for maximal removal of lead ion was determined using charred walnut shell (CWS) and xanthated walnut shell (XWS) at room temperature. A lead nitrate solution with a concentration of 25 ppm, adjusted to the optimal pH, was mixed with 25 mg of the adsorbent in separate bottles. The mixtures were agitated on a mechanical shaker at 200 RPM. Adsorption data were collected at regular intervals of time and the absorbance of the heavy metals before and after adsorption was determined using AAS.

2.5 Adsorption Kinetics

The kinetic study of lead ion adsorption was interpreted by the study of concentration changes of the filtrate at different time interval. Lagergren's two reaction models (pseudo-first and pseudo-second order) were applied to correlate the time-dependent percentage reduction in lead ion concentration for both CWS and XWS adsorbents. The kinetics of lead removal were further analyzed by graphical interpretation. The pseudo-first order kinetics is linearly represented as,

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad , \quad (3)$$

where, q_e is amount of metal adsorbed at equilibrium phase (mg g⁻¹), q_t is extent of metal ion adsorbed at any time (mg g⁻¹), K₁ is Lagergren's rate constant for first-order adsorption (min⁻¹).

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 amid heavy metal-ions and adsorbent. The formula of pseudo-second order kinetic is expressed as,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (4)$$

The validity of kinetic models can be investigated by studying the kinetics at different time intervals.

2.6 Adsorption Isotherm Study

The adsorption isotherm was constructed to delineate the equilibrium assembly among the extent of adsorbed lead ion to adsorbent mass and remaining unadsorbed material. For this, 25 mg of adsorbent was treated with 25 mL of lead solution with varying initial concentrations at optimal pH. The sealed bottle was agitated for 3 hours on a mechanical shaker at 200 RPM then allowed to attain equilibrium over 24 hours. The agitated sample was filtered and concentration was analyzed using AAS. The isotherm data were analyzed to understand the impact of initial lead ion concentration on the adsorption process, and the results were interpreted using appropriate adsorption isotherm models. In this study, Freundlich isotherm and Langmuir isotherm remained applicable to assess the adsorptive behavior of lead (II) on to the adsorbent.

The linear Freundlich isotherm equation is

$$\log q_e = \log K + \frac{1}{n} \log c_e, \quad (5)$$

where q_e = quantity of metal adsorbed per unit mass of adsorbent (mg/g),

c_e = concentration at equilibrium (mg/L),

K = adsorption constant,

n = Freundlich constant characteristic of adsorption system . Now,

$$\frac{c_e}{q_e} = \frac{1}{K q_m} + \frac{c_e}{q_m}, \quad (6)$$

where q_m = Mono-layer sorption associated Langmuir constant,

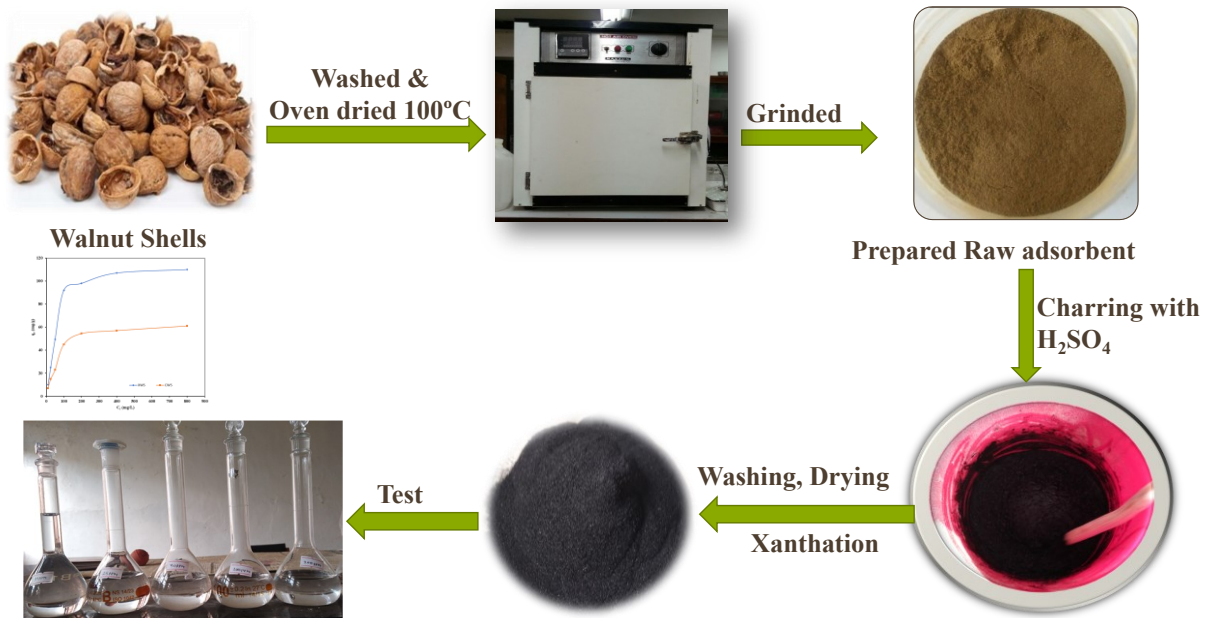
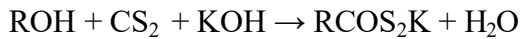
K = Langmuir equilibrium isotherm constant (L/mg) and represents enthalpy of sorption.

3.0 Results and Discussions

3.1 Synthesis of Adsorbent (by xanthation process)

The process of synthesis of the adsorbent materials is illustrated in the scheme 1. Lignocellulose is a major constituent of biomass which gets charred by the dehydrating action of concentrated sulphuric acid. Even if full carbonization is incomplete, partial carbonization can still lead to the formation of porosity in biomass. During this process, volatile impurities are driven off leaving behind the carbonaceous residue. This action develops porosity of various sizes with increased surface area.

In the xanthation process, the desired material with alcoholic functionalities is treated with alkali (like KOH) followed by carbon disulfide (CS_2) to introduce esters of dithiocarbonate ($RCOS_2^- M^+$), also known as xanthates. Firstly, the charred walnut was treated with 15 % KOH, then, treated by carbon disulfide to produce xanthated walnut powder (XWP). The alkoxide formed from potassium hydroxide acts as a nucleophile, reacting with the electrophilic carbon center of CS_2 .



Scheme 1: Preparation of adsorbent from waste walnut shell for the study of adsorptive removal of Pb(II)

If any remaining cellulose is present after charring, it reacts with carbon-disulphide in the presence of strong alkali such as KOH or NaOH to form K/Na-cellulose xanthate. The introduction of sulphur is anticipated to chelate metal-ions at the time of removal of heavy metal ions according to hard and soft acid-base (HSAB) principle. Here, a weak base sulphide ion reacts with weak acid lead ion to form stable compound, lead sulphide.

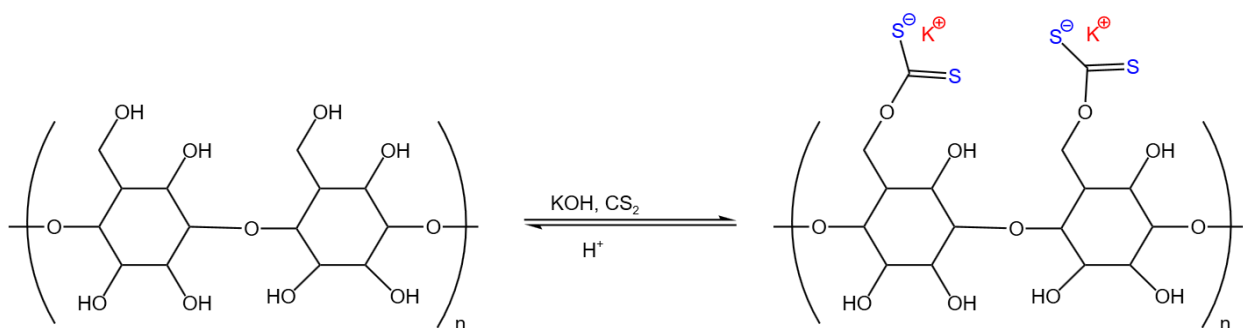


Figure 1: The mechanism of xanthation

3.2 Physicochemical Characterization

3.2.1 Crystallinity Study

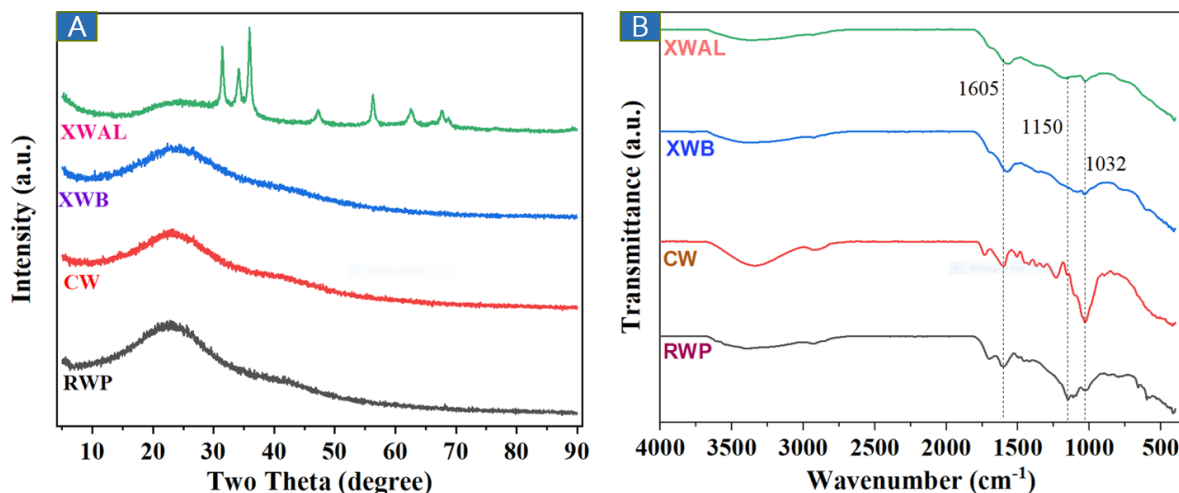


Figure 2: (A) XRD spectra and (B) FTIR spectra of various adsorbent materials at different conditions.

The X-ray diffraction pattern of synthetically activated carbon materials is depicted in Fig.2A. The broad peak between 15–30° indicates the predominantly amorphous nature of materials. There is no significant change in crystallinity of the materials upon charring and xanthation. Following lead absorption, xanthated activated carbon exhibits a strong peak at 30–31° and a peak of relatively low intensity at ~62°, indicating Pb(II) adsorption from the solution. These peaks could be associated with the formation of lead sulphide due to the interaction of lead(II) ions and sulphide of xanthated mass. The peak position of lead sulphide is in agreement with other reports (Wattoo et al., 2012).

3.2.2 Functional Group Study

The FTIR spectra of several phases of walnut powder are shown in Fig.2B. The –OH stretching of phenolic or carboxylic functionality or adsorbed water groups is thought to be the cause of the peak at around 3200–3600 cm^{-1} . The symmetric stretching of the –COOH group, aromatic C=C vibrations, and hydrogen-bonded carbonyl groups are responsible for the peak at 1605 cm^{-1} (Praipipat et al., 2023). During xanthation process, carbon disulphide reacts with hydroxyls group present in cellulose chains to produce cellulose xanthate. This involves the substitution of oxygen atom in hydroxyl group with Sulphur atom from carbon disulphide. In the FTIR, this is clearly indicated by the diminishing of IR band at 1730 cm^{-1} (–C=O group) when charred walnut (CW) is introduced to xanthate on process (XWB). Xanthation utilizing KOH in the presence of CS_2 produces oxidized carbon, such as C-O- stretching or S=O stretching, as indicated by a wide peak seen between 1000 and 1300 cm^{-1} . An intense absorbance band at ~1032 cm^{-1} of CW could be associated with the carbon to sulphur bond consequence due to sulphuric acid charring. This finding is in agreement with those of other reports (Vorobyev et al., 2019). These results demonstrate that the manufactured walnut powder underwent xanthation successfully.

3.2.3 Surface Morphology Study

The surface of the as-prepared material was studied using field emission scanning electron microscopy (FE-SEM). The FE-SEM image of raw walnut powder (RWP), charred walnut (CW) and xanthated walnut powder (XWP) at different magnification are displayed in Fig.3. The carbonizing process of fresh walnut shell produces porosity and xanthation progression produces cellulose xanthates in presence of alkali. The sulfur atoms captures Pb(II) ion according to HSAB

principle. Through elemental mapping, the EDX data revealed the presence of carbon, sulfur, and potassium (Fig.4). Oxygen could exist in the form of oxides. The effective xanthation process was validated by the elemental mapping which is in consistent with FTIR analysis.

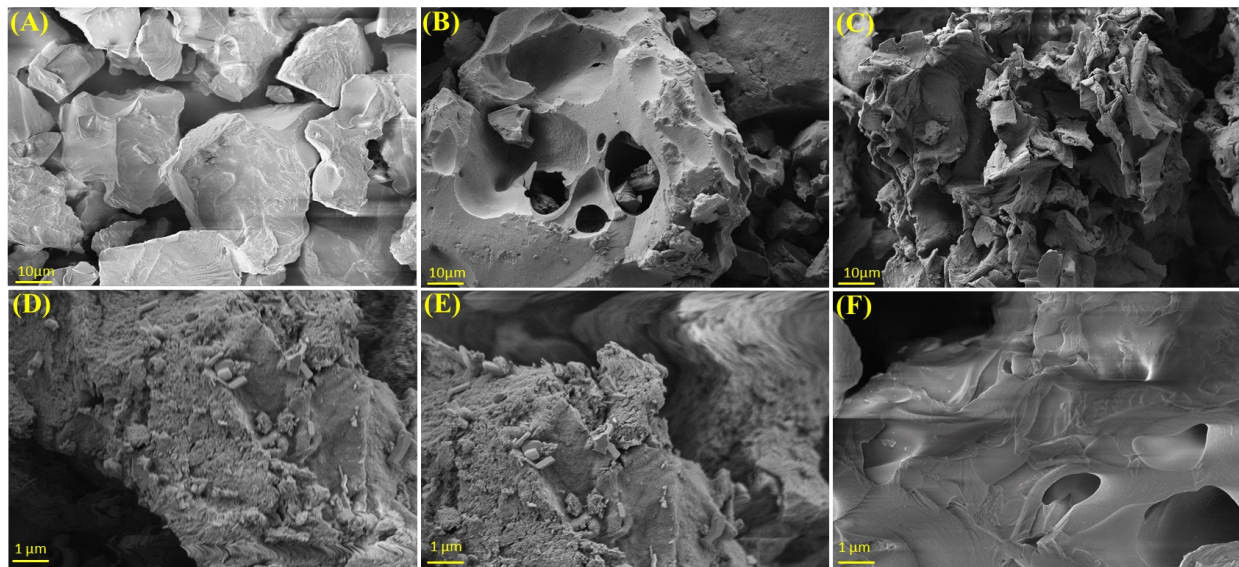


Figure 3: FE-SEM image of Raw Walnut Powder (A and D), Charred Walnut (B and E), and Xanthated Walnut Powder (C and F) under magnifications of 1000X (scale 1 μm) and 5000X (scale 10 μm) respectively.

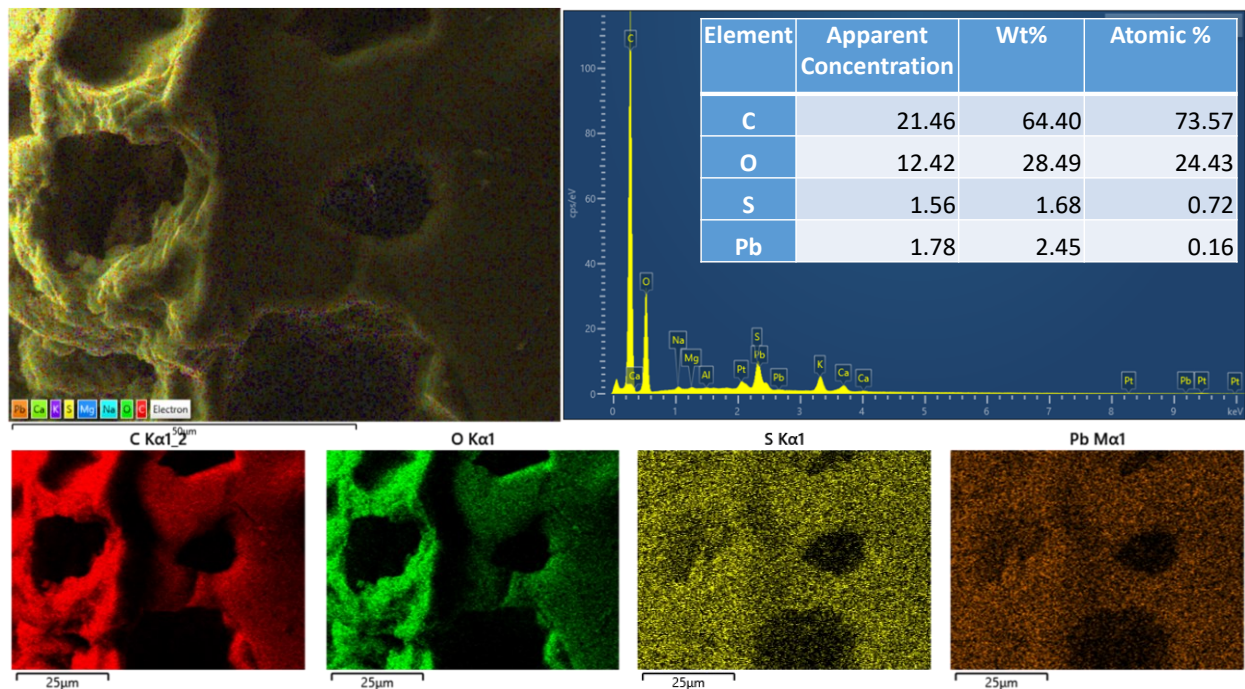


Figure 4: EDX spectra with mapping of elemental composition of as-synthesized xanthated carbon after lead (II) removal.

3.3 Adsorption Study

The adsorption study looked at how lead removal was impacted by pH, contact time, and initial concentration. With both the initial concentration and the duration of contact with the modified

walnut shell, a greater proportion of lead was removed. A calibration curve was developed for the determination of Pb(II) ions using lead nitrate solutions with concentrations of 0.25, 0.5, 1, 2, and 4 ppm. Fig.5A curves enable the standard addition and dilution approach to test Pb(II) directly within a quantifiable range.

3.3.1 Effect of pH

For charred walnut shell (CWS) and xanthated walnut shell (XWS), the effect of pH on the adsorption process and its effectiveness was examined (Fig. 5B). Each bio-adsorbent's adsorption investigation was done individually, using pH ranges from 1 to 9. The pH 4 was ultimate pH for lead ion adsorption. The proportion of lead ions removed by CWS at this pH rose from 7.96 % at pH 1 to 73.2 % at pH 4, then fell to 48 % at pH 9. Similar trends were seen with XWS, where the percentage removal rose from 24 % at pH 1 to 98 % at pH 4, then fell to 70 % at pH 9. The optimal pH for lead ion adsorption by CWS and XWS is 4.0 and the maximum percentage

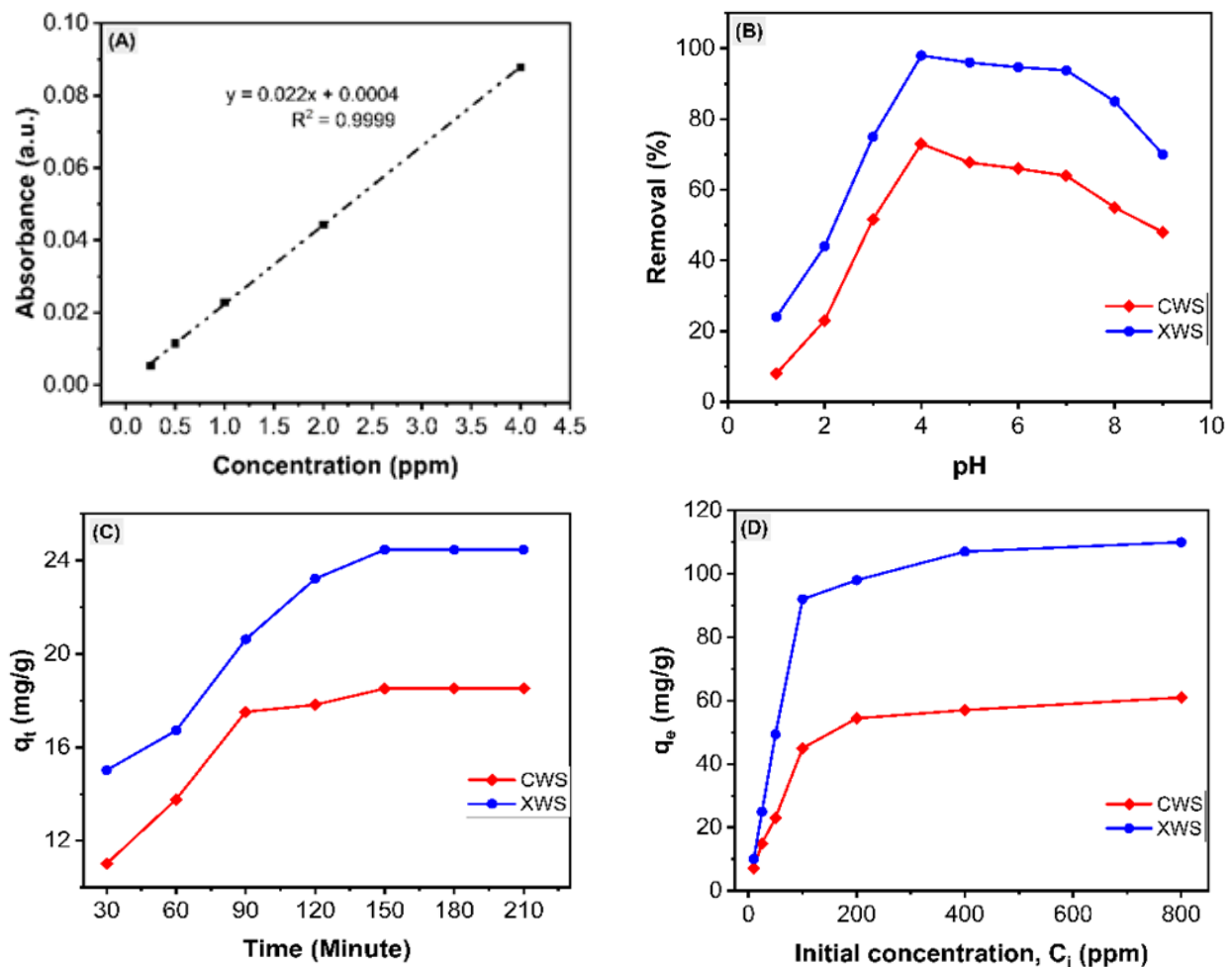


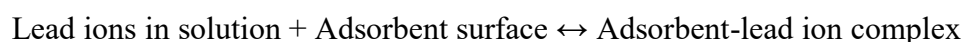
Figure 5: (A) Calibration curve: Absorbance versus concentration of Pb(II) in ppm, (B) Effect of pH, (C) Effect of contact time, (D) Effect of initial concentration on the adsorption of Pb(II) by CWS and XWS.

removal of the lead metal ion were found to be 69.2 % and 98 % respectively. At the lower pH, the adsorbent surface gets protonated and there are less adsorption sites for lead (II) adsorption. At higher pH, Pb(II) gets precipitated in the form of hydroxide. So, on either side of pH 4, removal efficiency of the adsorbent is diminished. The percentage adsorption did, however,

initially rise to pH 4, at which point it began to fall. Due to the existence of additional adsorption sites in xanthated walnut shell (XWS), it demonstrated a greater percentage of adsorption than charred walnut shell (CWS). As a result, commercial activated carbon is viewed as being inferior to XWS as an alternative adsorbent.

3.3.2 Effect of Contact Time

In batch adsorption investigations, interaction interval is a crucial variable. At various time points, the adsorbate absorption by CWS and XWS was examined. Fig.5(C) illustrates that the equilibrium contact time for Pb(II) adsorption by CWS and XWS, achieving uptakes of 18.92 mg/g and 24.46 mg/g, respectively, was reached within 150 minutes at pH 4. Initially, rapid metal sorption occurs with longer contact periods, leading to a gradual increase in Pb(II) sorption efficiency before reaching a plateau. This phenomenon is attributed to the abundant surface area or active sites available for adsorption, coupled with high concentration gradient of lead ions in the solution, facilitating increased lead adsorption over time. The adsorption process involves a multi-step mechanism, including transportation of lead ions to the adsorbent surface from the bulk solution followed by diffusion within the porous structure, and adsorption on to active sites. The reaction can be represented as follows:



The adsorption rate decreased and stayed constant when equilibrium condition was reached, as it became harder to occupy the remaining surface area. The equilibrium time required for complete adsorption depends on various factors, including initial concentration of lead, specific surface area of the adsorbent material, and diffusion characteristics within the porous structures. Overall, during this optimal period, chemically treated XWS demonstrated greater metal uptake than CWS. This could be associated with the good interaction between sulphide group of XWS and Pb(II) ions as per HSAB principle. Herein, Pb(II) ion serves as soft Lewis acid due to large ionic radii with low charge density and sulphide ion serves as soft Lewis bases due to large ionic radii with high polarizability. This interaction is favorable for stable combination. In case of CWS, no such strong affinity occurs as in XWS and extent of adsorption is low.

3.3.3 Effect of Initial Concentration

Chemically altered walnut shell (CWS) and xanthated walnut shell (XWS) were utilized to investigate the impact of starting concentrations on the adsorption of Pb(II) at ideal pH level of 4. The aqueous solution's concentration ranged from 10 mg/L to 800 mg/L. The plot of q_e vs c_i for the adsorption of Pb(II) is shown in the Fig.5(D). According to the testing results, CWS and XWS had maximal adsorption capabilities of 61 mg g⁻¹ and 110 mg g⁻¹, correspondingly. When compared to CWS, XWS showed a greater capability for adsorption. The figure shows that when the gradient of the starting concentration rises, the sorption capacity also rises. At a lower starting concentration, the rate of adsorption is determined by the metal ions in the domain of enough sorption sites while at higher initial concentrations, the rate of adsorption is determined by the adsorption sites in the domain of large number of ions in queue.

Figure 5(C) demonstrates the equilibrium contact time required for the adsorption of Pb(II) by CWS and XWS, achieving uptakes of 18.92 mg g⁻¹ and 24.46 mg g⁻¹, individually, within a span of 150 minutes under pH 4 conditions. Initially, there is a rapid uptake of metal ions as the contact time increases. This rapid sorption process is followed by a gradual enhancement in the efficiency of Pb(II) sorption until it reaches a plateau. This observed trend can be attributed to

the availability of ample surface area or active sites on the adsorbent materials. Additionally, the significant concentration gradient of lead ions in the solution contributes to the initial rapid adsorption of lead, which progressively slows down as equilibrium is approached. The abundance of active sites and the intensified concentration gradient facilitate the continuous adsorption of lead over time until saturation is reached, ultimately leading to a plateau in sorption efficiency.

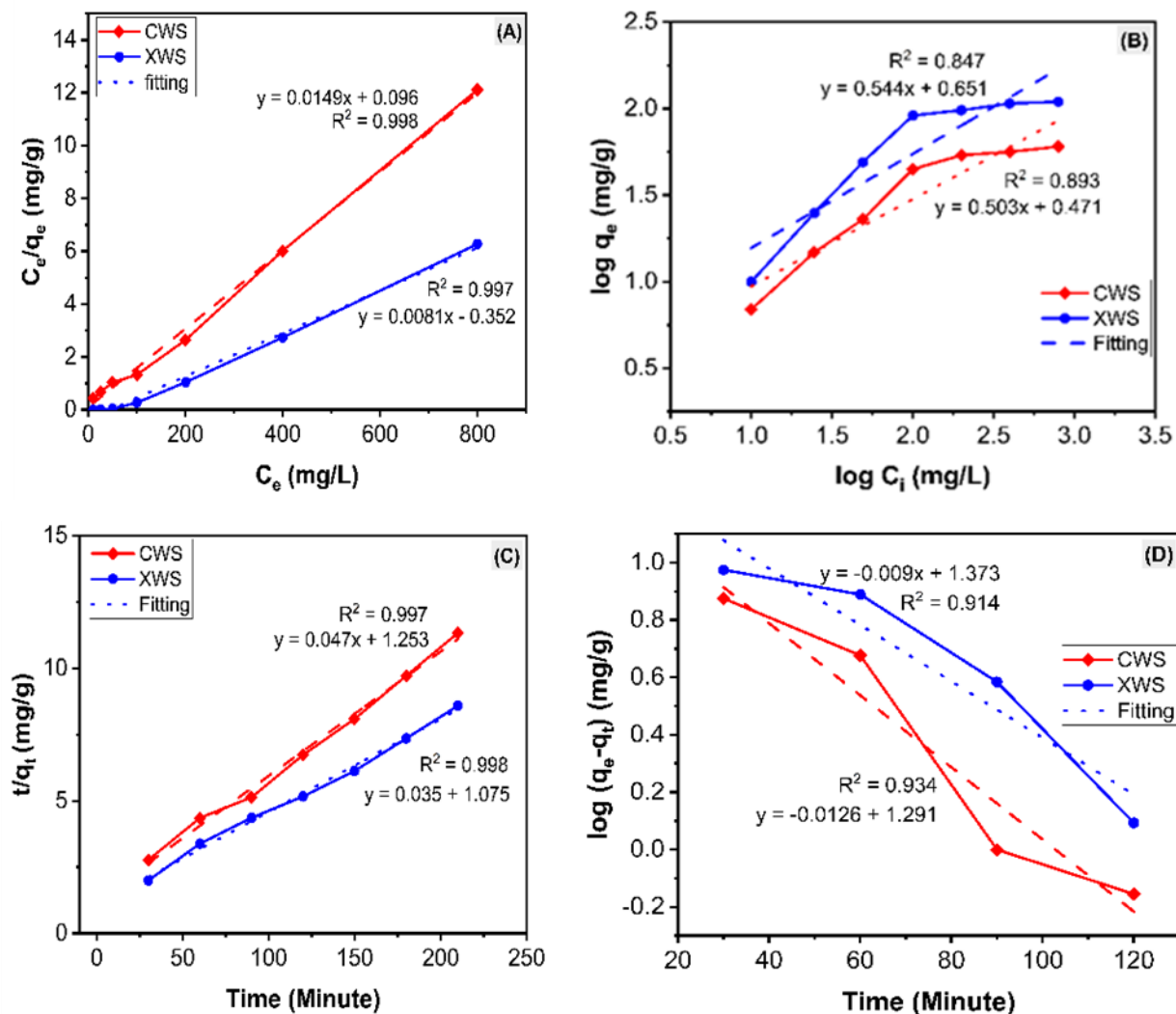


Figure 6: Adsorption study (A) Langmuir isotherm, (B) Freundlich adsorption isotherm, (C) Pseudo-second order kinetics model and (D) Pseudo-first-order kinetics model for adsorption of Pb(II) on to CWS and XWS

3.3.4 Adsorption Isotherm Studies

The adsorption mechanism between adsorbate and adsorbent system is nicely explained by adsorption isotherm which can be analyzed using different isotherm equation like Langmuir and Freundlich isotherm equation. The best-fit isotherm model illustrates the adsorption of metal ions.

Figure 6(A) spectacles the linear graph of c_e/q_e versus c_e with a goodness of fit value 0.998 for Pb(II) adsorption on to CWS and 0.997 for Pb(II) adsorption on to XWS, respectively. Here, the maximum adsorption capacity for both XWS and CWS were 109.90 and 61.01 mg/g, respectively as given in Table 1. Result shows that the Pb(II) adsorption process is favorable and

adsorption data fit well in the Langmuir adsorption isotherm. Furthermore, to test the fitness of Freundlich adsorption model, a graph of $\log q_e$ versus $\log c_i$ was plotted (Fig. 6 B). The goodness of fit (R^2 value) for Pb(II) adsorption on to CWS and XWS were found to be 0.893 and 0.847, respectively. These values do not support the linearity of the line for 95% confidence level. Therefore, Pb(II) adsorption on CWS and XWS follows Langmuir adsorption isotherm model.

Table 1: Langmuir and Freundlich parameter for the adsorption of Pb (II) onto CWS and XWS

Pb(II) adsorption	Langmuir parameter		Freundlich parameter	
	q_e (mg/g)	R^2	q_e (mg/g)	R^2
Pb(II) onto CWS	61.01	0.998	61.01	0.893
Pb(II) onto XWS	109.9	0.997	109.9	0.847

3.3.5 Batch Kinetics Study

The adsorption of Pb(II) on to CWS and XWS were studied using different kinetic models such as pseudo-first order and pseudo-second order kinetics. The graph of T/q_t against time (Fig. 6 C) conceded straight line with high correlation coefficients (R^2) of 0.997 and 0.998 for CWS and XWS adsorbents, correspondingly. The equilibrium concentration (q_e) for the adsorbents were found to be 18.25 and 24.44 mg/g, respectively for CWS and XWS. This specifies that adsorption progression trails the pseudo-second order reaction. Plot of $\log (q_e - q_t)$ vs. time for the pseudo-first order kinetic model was also examined and displayed in Fig.6(D). In this case, the goodness of fit (R^2) value for the adsorption of Pb(II) onto CSW and XWS are 0.914 and 0.934, respectively (Table 2). Higher correlation coefficients for both adsorbents were produced by the pseudo-second order model, which was compared to have a superior match. Based on the obtained results, it can be revealed that the kinetic data for adsorption of lead onto CSW and XWS were found with best fitting with high correlation coefficient value for pseudo-second order reaction.

Table 2: Pseudo-first-order kinetics model for adsorption of Pb(II) onto CWS and XWS

Adsorbents	Pseudo-first order			Pseudo-second order		
	Slope	q_e (mg/g)	R^2	Slope	q_e (mg/g)	R^2
CWS	-0.0126	18.92	0.934	0.047	18.92	0.997
XWS	-0.009	24.44	0.914	0.035	24.44	0.998

3.4 Functionalization of Adsorbent and Mechanism of Adsorption

During charred walnut shell (CWS) preparation, porous structure develops with a sizable surface area. Different functionalities like carboxyl (-COOH), hydroxyl (-OH), and phenolic groups are existent on its surface, acting as binding sites for lead ions. The surface of CWS gets protonated at lower pH levels, which increases the concentration of positively charged sites. The lead ions present in the solution are electrostatically drawn to and bound by these positively charged sites, increasing the CWS's ability to adsorb them. The binding of lead ions through ion exchange or complexation reactions is generalized as:

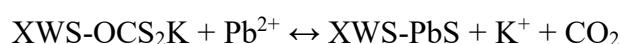


In this reaction, the hydroxyl groups (-OH) on the surface of CWS interact with Pb^{2+} ions in the solution, leading to the formation of the adsorbate complex (CWS-Pb^{2+}).

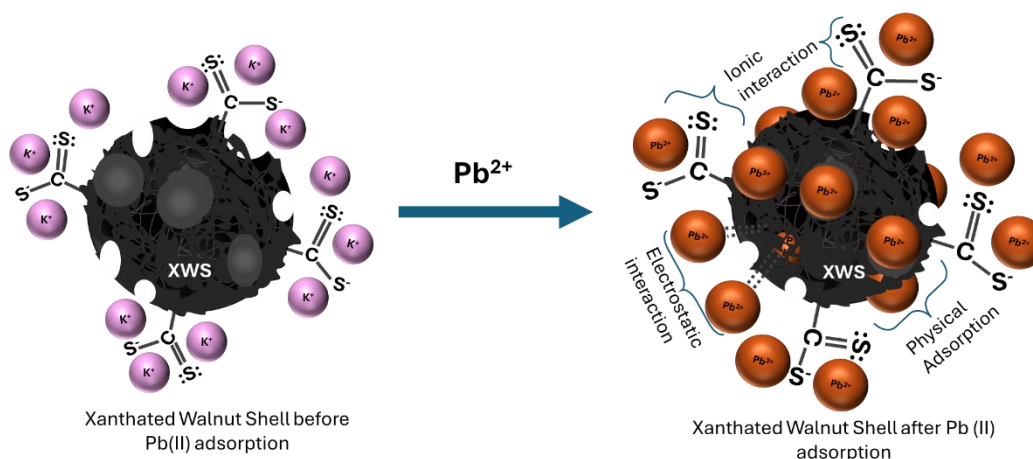
Since the xanthation process of walnut shell with an alkali (KOH) and CS₂ introduces sulphur group in the carbon surface the hydroxyl groups on the walnut shell's surface are changed during this process into xanthate groups (RCOS²⁻), which has a great affinity for metal ions like lead. The adsorbent's surface gains sulfur-containing functional groups during the xanthation process, and these groups can chelate with metal ions based on HSAB principle. The surface functional groups on XWS are protonated at lower pH levels to enhance the positive charge density, which aids in the electrostatic attraction and binding of lead ions to the XWS surface. The xanthated (sulphur-containing functional groups) walnut shell can chelate with metal ions like lead as illustrated in the reaction below:



In this reaction, the hydroxyl groups (-OH) on the surface of walnut shell reacts with carbon disulfide (CS₂) in the presence of potassium hydroxide (KOH) to form xanthate groups (XWS-OCS₂K). These xanthate groups have a strong affinity for metal ions. The adsorption of lead onto the XWS surface can be represented by the following reaction:



In this reaction, the xanthate groups on the XWS surface chelate with Pb²⁺ ions, leading to the formation of lead sulfide (XWS-PbS) on the adsorbent surface. Here, sulphide ion acts as soft base and lead (II) acts as soft acid. According to HSAB principle, the interaction between soft acid and soft base is strong enough to hold it (Rathore et al., 2017).



Schematic 2: Mode of adsorption of Pb(II) on the XWS surface

In both CWS and XWS, positively charged regions on the adsorbent surface promote lead ion attraction and binding through electrostatic interactions at lower pH levels as shown in schematic 2. Consequently, lead removal's adsorption capability is boosted. The precise processes and surface chemistry of CWS and XWS, however, may differ from one another due to XWS's extra chemical change during the xanthation process.

4.0 Conclusion

In conclusion, this study highlights the efficacy of walnut shells and their modified form as promising bio-adsorbents for Pb(II) removal from water. Extensive experimental investigation revealed that the optimal pH conditions achieved at pH 4, for both charred walnut shells (CWS)

and xanthated walnut shells (XWS). Equilibrium was attained within 150 minutes, with maximum adsorption capacities of 61.03 mg g⁻¹ for CWS and 109.9 mg g⁻¹ for XWS. The experimental findings were found to be best described by the Langmuir adsorption isotherm which shows monolayer adsorption on to the surface of adsorbents. Additionally, kinetic analysis favored the pseudo-second order model, suggesting chemisorption as the predominant adsorption mechanism. These findings underscore the potential of walnut shells as cost-effective and environmentally friendly alternatives for mitigating Pb(II) contamination in water systems. Further research could explore optimization strategies to enhance adsorption efficiency and investigate the scalability of walnut shell-based adsorbents for real-world applications.

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Declaration of Interests

The authors declare that they have no known conflicts of interest or personal relationships that could potentially influence the work reported in this paper.

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