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Original Research Article

Adsorption of Lead Ions from Wastewater Using Raw and Nano Composite from Agro Waste of *Spondias Mombin*

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Abstract

Treatment of wastewater from heavy metal pollutants still remains a serious challenge for some developing countries without centralized waste water systems. The study examines the potentials of raw and nano composite from *Spondias mombin* seed as an adsorbent for removal of lead (II) ions from contaminated water. Instrumental techniques such as scanning electron microscopy (SEM), Fourier Transform Infrared Spectrophotometer (FTIR), and Atomic absorption Spectrophotometer (AAS) were used to characterize the absorbents. The study analyzed the effect of various factors including absorbent dosage (0.2 – 1.0g), lead concentration (100-300 mg), contact time (30-180 min), pH (2-10) and temperature (30-50°C) respectively, on the absorption of pb^{2+} ions. The experimental findings revealed that the adsorbents have high absorption capacity and high percentage removal for the removal of pb^{2+} ions from aqueous solutions. Absorption isotherm kinetic models and thermodynamic studies were applied to access the absorption mechanism of lead (II) ion removal. The Langmuir absorption isotherm and pseudo-second-order model were found to fit the equilibrium data for nano composite while Freundlich isotherm and pseudo-first-order fitted the equilibrium data for raw fruit. According to the results obtained, a linear model was generated which indicated good predictability and the results agreed with the experimental data. The contact time and absorbent dosage were predicted to have a positive effect on the absorption process. However, after the investigation on the efficiency of raw and nano composite of *Spondias mombin* fruit on the removal of lead (II) ion from aqueous solutions as the impact of different variables were investigated. The study showed that the raw and modified adsorbents can be considered effective adsorbent for the removal of lead metal ions from wastewater by varying some basic parameters. The physiochemical properties of the absorbent were analyzed and the results obtained confirmed the adsorption potentials of the raw and nano composite. The removal efficiencies of both adsorbents on the Pb^{2+} ion were strongly dependent on their contact time, initial metal ion concentration, absorbent dosage, pH and temperature. The Langmuir isotherm model was well fitted to the experimental data, indicating that the two absorbents were effective in removing Pb^{2+} ions from aqueous solutions with low absorption energy. The experimental data of Pb^{2+} ions adsorption by raw and nano composit adsorbents studied were fitted with the pseudo-first-order and pseudo-second-order kinetic model respectively, revealing that adsorption occurs by physiosorptions and chemisorptions technique. The thermodynamic data showed that the adsorption process was exothermic, spontaneous and feasible in nature. Therefore, this work exposed the possible removal of lead (II) ions by raw and nano composite from agro waste of *Spondias mombin* from wastewater, which is generally a low cost agro waste.

Keywords: Lead, Wasterwater, Raw and Nano Composite, Adsorption, *Spondias mombin*.

1. INTRODUCTION

Fresh water has been the most essential element needed by humans and aquatic eco-system. Fresh water when contaminated by industrial effluents alters the biological, chemical and physical properties of fresh water. This alteration is as a result of effluents characterized with heavy metal which are non-biodegradable in nature and also considered very harmful to health when accumulated and exposed for too long in the body (Lakam and Gremu, 2021). This situation leads to increase of heavy metals in surface and ground waters which also affects aquatic bodies (Bayow *et al.*, 2022). Frequently pollutants in freshwater are heavy metals, the major concern to researchers is the frequent occurrence of untreated wastewater containing heavy metals in the environment which are dengerous to both plants and animals (Kuibir *et al.*, 2018).

Globally, lead metal is mostly found in the environment and they are highly dangerous to health (Demay *et al.*, 2018). Lead (II) ions are mostly present in industrial effluents such as batteries, miners, paint, pesticides, smelting and electroplating industries. When lead is accumulated in the body due to exposure to contaminated water and other sources it causes health issues like hypertension, impaired blood pressure, stomach aches, kidney and brain damage and most times may lead to miscarriages in pregnant women (Bayuo *et al*., 2019). The world health organization (WHO) desired limit of lead (Pb) concentration in drinking water is 0.01 mg/L (Ahmed *et al.*, 2003). To prevent heavy metal pollution and limit constant human poisoning, heavy metal contaminated wastewater must be treated before discharging them in the environment (Ahmedi *et al*., 2014).

Several methods have been investigated for removal of heavy metals from waste water before discharging it to the environment (Ullah *et al*, 2020). These methods probed for heavy metal removal include coagulation, flocculation, chemical precipitation, membrain filtration, ion exchange and electrochemical techniques (Yadar, *et al*., 2021). Many of these removal techniques showed good results but they have low ion removal efficiency, expensive, can easily generate secondary pollutants, high energy requirements and high sludge formation (Ranjan *et al.*, 2018). Therefore, researchers are focusing on developing cheap and efficient methods for treating heavy metal polluted wastewater. Adsorption was showed to be the most efficient unit operation for the removal of hazardous heavy metals from wastewater solutions (Guratilake, 2015). This is as a result of its outstanding features like design and operation simplicity, toxic pollutant insensitiveness, cost effectiveness, high heavy metals sorption efficiency and negligible sludge formation (Lasheen *et al.*, 2017). Raw and nano composite are the most utilized and recognized heavy metal adsorbent. It has proven to be more advantageous in heavy metal removal because of its high rate of removal efficiency, high metal uptake capacity and ease of working principle (Lekara *et al*., 2021).

For the past few decades, heavy metal removal methods have brought a great challenge to researchers both local and international, more especially in developing countries (Chai *et al.*, 2021). Currently, agro waste has been considered one of the best sources of inexpensive adsorbents that are attracting scientific interest for heavy metal removal due to its availability and abundance, biodegradability in natural and environmental settings, high surface area, easily renewable, higher ability to absorb metal ions, compatibility, eco-friendly and more specific in nature (Gupta *et al.*, 2021, Elgraly *et al.*, 2021).

Agro waste of *Spondias mombin* is made up of various functional groups like carboxyl groups, phenol, hydroxyls, amides, ethers, and methyl and amines that can act as binding sites on their surfaces to which the metal ions can be effectively adsorbed under normal circumstances through various mechanisms (Bilal *et al*., 2022, Nleonu *et al*., 2017). Several agricultural wastes such as rice husk, peanut husk, sawdust, groundnut husk, potato peels, banana peels and sugar cane bagasse have been studied (Simon *et al.*, 2023, Tsade *et al.*, 2020). *Spondias mombin* or yellow mombin is decous with a dense and spreading crown and grows up to 25m tall and at least 60 cm in trunk diameter. It is from the family of anacardiaceae, the bark is thick, and the leaves are compound comprising five to nine pairs of leaflets. The flowers occur on terminals stalks. The fruits, small and yellow have leathery skin and thin layer of pulp and single seeded. The pulp can be eaten fresh or made into desserts or juice. The young leaves are consumed raw or cooked. The seeds are also edible. Root ashes are used in making soap. The wood is used for posts, boxes, matches, general carpentry, tool handles etc. (Chittendon, 1956, Dave, 2015, Eric, 2016). *Spondias mombin* seed has been identified to contain high amount of saponins, alkaloids, flavonoids, tannins and cyanogens glycosides (Ali *et al.*, 2014). Sp*ondia*s *mombin* is used by the local population to treat diseases due to its many biological properties, such as antiviral, anti-inflammatory, antioxidants and anti-bacterial properties (Ana *et al*., 2022).

Furthermore, the selection of a nano adsorbent is very important in removal of heavy metals from wastewater through complexation or electrostatic attraction between metal ions and adsorbent surface. A nano adsorbent is a type of nano material with high adsorption capacity that is chemically active. It includes carbon-based nano particles, metal and metal-oxide (Deeksha, 2023). The study focuses on the adsorption of lead (II) ion from wastewater using raw and nano composites from agrowaste of spondia mombin fruit as influenced by dosage, contact time, initial metal concentration pH and solution temperature. The results of the experiment were extended to the study of isotherms, kinetic and thermodynamic, parameters for the lead (II) ion adsorption processes.

2. MATERIALS AND METHODS

2.1. Chemical and Reagents

Analytical grade reagents were used in this study. Stock solutions of 2000 mg/l of lead (ii) ions were prepared using deionized water by dissolving the required amounts of $PbCl_2$ (a product of loba chemie PVT ltd, India). The corresponding dilutions used in the adsorption experiment were prepared from the stock solution.

2.2 Preparation of Adsorbent (Raw and Nano Composite)

Spondias mombin seeds were collected from the botanical farm of the Federal Polytechnic, Nekede Owerri, Imo State. The fruits were first washed thoroughly with running water, followed by distilled water to remove extraneous materials, and air dried for 16 days. The dried material had it seeds removed leaving the shell. The shell was grounded into powder. The powered samples were separated into two portions, of which one was used to prepare copper nano composite.

2.2.1 Extraction of *Spondias Mombin* Shell

Sixty Five 65 (g) of sun dried shell of *Spondias mombin* were grounded to semi powder for a period of one week after which only 50g of the grounded shells were put in a Soxhlet extractor fitted with a reflux condenser and extracted with 250 ml of ethanol for 12 h. The ethanol extract was recovered using rotary evaporator leaving behind the gel. The solid residue of 10g obtained was re-dissolved in ethanol/water mixture (4:1) and filtered. The filtrate was used without further purification for the preparation of copper nano composite.

2.2.2 Synthesis of Copper Oxide Nano Particles (CuO NPs) Using *Spondias Mombin* Extract

Copper oxide nano particles were obtained by combining the extracted *Spondias mombin* shell in a 1:9 ratio with a 1 mM concentred anhydrous copper sulfate solution. The mixture was stirred at room temperature for two hours. CuO NPs were synthesized the colour of the solution changes to brown. After 24 h of incubation, the colloidal was centrifuged at 10,000 rpm for 10 min to obtain a pellet, which was then purified by washing three to five times with double distilled water. The final residue obtained was calcinated in a muffle furnace at 400 ^{o}c to remove the attached organic matter of plant. The powdered substance is stored for further analysis (Zahrah, 2022).

2.2.3 Preparation of Nano Composite

2 g of Polyvinyl alcohol (PVA) was dissolved in 50 ml of water on heating, after complete dissolution, 2 g synthesized CuO NPs were added. Then it was dispersed using magnetic stirrer for 3 hrs at 50 ^{o}c. The solution was poured into petridish and the solution was evapourated at 55 ^{o}c overnight to cast into film. The obtained film was stored in the desiccators to keep out of moisture (Manimozhi *et al.*, 2020)

2.3 Adsorbent Characterization

The mineral content of the adsorbents were determined using atomic adsorption spectrophotometer (AAS). The functional groups present on the surface of the raw adsorbent were determined using fourier transform infrared (FTIR) spectroscopy (Happ-Genzel). The surface morphology of the raw adsorbents were studied with the help of a scanning electron microscope (Phenom Prox) and prevailing quantitative characterization of particle size and surface area of adsorbent was achieved using x-ray diffraction (XRD).

2.4 Adsorption Study

2.4.1 Effect of Contact Time

The adsorption studies were performed with each adsorbent and metal ions separately, using 100 ml of metal solution. The initial concentration of 250 mg/l was stirred with 0.2 – 1.0 g of adsorbents. After 30s min interval, the mixtures were filtered, and the filtrates were analyzed for the unadsorbed lead metal ions using an atomic absorption spectrophotometer (AAS).

2.4.2 Effect of Adsorbent Dose

Batch studies on the effect of adsorbent dose on the removal efficiency of the adsorbents were also studied. The adsorbent was mixed with 250 mg/l of lead and metal solution at various doses of 0.2, 0.4, 0.6, 0.8 and 1.0 g respectively, in 100ml of metal solution and stirred for 30 min.

2.4.3 Effect of Initial Metal Ion Concentration

The effect of an initial metal ion concentration on the adsorption efficiency of adsorbents were examined in this experiment. The study was performed by preparing different concentrations of metal ions. The adsorbents were mixed with a synthetic aqueous solution of lead metal concentrations of 100, 150, 200, 250 and 300 mg/l, respectively, and was agitated continuously at a constant contact time of 30 min and adsorbent dose of 0.2 g. The volume of the synthetic aqueous solutions were measured in 100 ml each.

2.4.4 Effect Temperature

Temperature is another variable that affect the metal adsorption process. The impact of temperature on the adsorption of Pb ions in the solution was demonstrated. Lead ions were removed from the aqueous solution at different temperature ranges of 30, 40, 50, 60, and 70 ℃ using a constant dosage of 0.1 g/100 ml of 40 mg/l Pd solution for 60 min.

2.4.5 Effect of pH

The impact of pH on lead ion adsorption was investigated on five different pH solutions 2, 4, 6, 8 and 10.

2.4.6 Determination of Adsorption Efficiency and Capacity

The percentage adsorption efficiency (A %), and the adsorption capacities (qe) were calculated from the following equations:

$$A\ \% = \frac{Co - Ce}{Co} \times 100 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$qe\ (mg/g) = \frac{(Co - Ce)V}{m} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where Co and Ce (mg/l) are the initial and final concentrations of Pb^{2+} ions in solution respectively, V (L) is the volume of solution, and M (g) is the adsorbent mass.

2.4.7 Adsorption Isotherm Studies

The study applied Langmuir and Freundlich isotherm models to ascertain the adsorption capacity of the adsorbents. The adsorption isotherm models demonstrate a correlation between the amounts of Pb^{2+} ion in solution with the adsorbents. In the present study, Langmuir and Freundlich models were evaluated. The Langmuir isotherm explains single layer adsorption with adsorbent activated sites, whereas the Freundlich model is applied to heterogeneous surfaces with adsorption of multi-layer. The Langmuir and Freundlich adsorption isotherm equilibrium parameters were calculated using the equations below.

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$\log_{qe} = \log K_f + \frac{1}{n} \log Ce \quad (4)$$

Where q_m and K_L are the Langmuir constants (mg/g), K_f are Freundlich equilibrium constant (mg/g), qe is the metal dose adsorbed on a specific amount of adsorbent (mg/g), Ce is the equilibrium concentration of the solution (mg/l) and q_m is the maximum dose of metal concentration required to form a monolayer (mg/g).

2.4.8 Adsorption Kinetic Modeling

The degree of adsorption as a function of contact time was utilized to study the kinetics of Pb^{2+} ion adsorption from an aqueous solution. The adsorption kinetic modeling data was analyzed for each adsorbent, using pseudo-first-order and pseudo-second-order models. The pseudo-first-order and pseudo-second-order parameters were obtained using the following equations.

$$In \frac{C_t}{C_o} = - K_1 t \quad (5)$$

$$\frac{1}{C_t} = \frac{1}{C_o} + K_2 t \quad (6)$$

Where C_o is the initial concentration and C_t is the residual metal ion concentration of metal ion (mg/l) at a definite time t (min), K_1 is the pseudo-first order rate constant (min^{-1}), and K_2 is the pseudo-second order rate constant (mg/g.min).

2.4.9 Thermodynamic Studies

This study investigates the influence of solution's temperature on the adsorption of Pb^{2+} ions by both adsorbent at different temperatures (303, 308, 313, 318 and 323 K). The thermodynamic parameters of entropy (ΔS^o), enthalpy (ΔH^o) and Gibb's energy (ΔG^o) were evaluated to determine the viability, exothermic or endothermic nature and spontaneity of the adsorption process using the equations respectively.

$$\Delta G^\circ = -RT\ln K_d \quad (7)$$

Where K_d, T and R are the equilibrium rate constant (g/l), temperature (K) and gas constant (KJ/mol), respectively. The parameters of thermodynamic were calculated using equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the Adsorbents

The surface morphology of raw and nano composite of *Spindias mombin* fruit adsorbent was examined using scanning election microscopy. Figure 1a-1d displayed SEM image of the adsorbent before and after adsorption of Pb^{2+}. The SEM images shows that the raw and nano composite after adsorption of Pb^{2+}. The SEM images shows that the raw and nano composite derived from *Spondias mombin* fruit adsorbent has pores and rough surfaces. These holes and fibrous surfaces of the adsorbent were observed to cause the high adsorption of Pb^{2+} ion which were seen after the absorption of lead (II) ion. The significant changes were seen on the surfaces of the adsorbent after adsorption of lead ion. These results revealed that raw and nano composite particles derived from the *Spondia mombin* plant have enough actual surface area and binding centers to adsorb lead (II) ion.

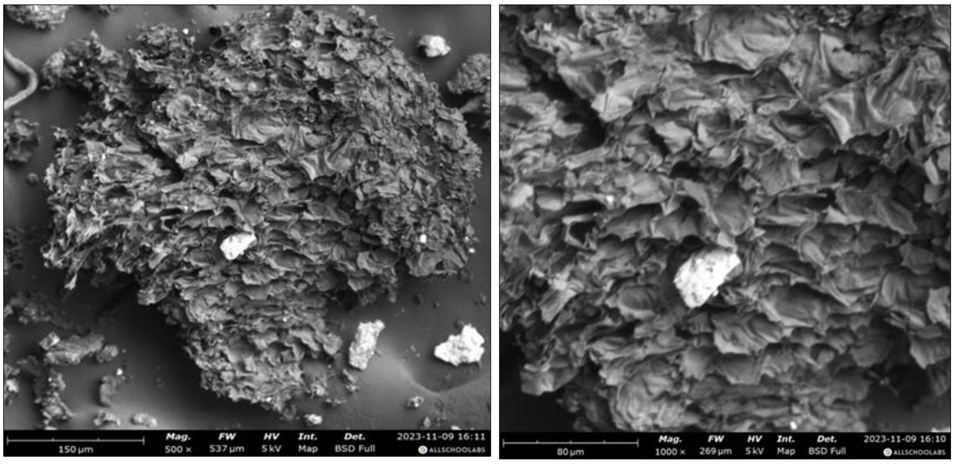

Figure 2a and b: depicts the SEM spectrum for raw and nano composite of *Spondias mombin* fruit before and after adsorption

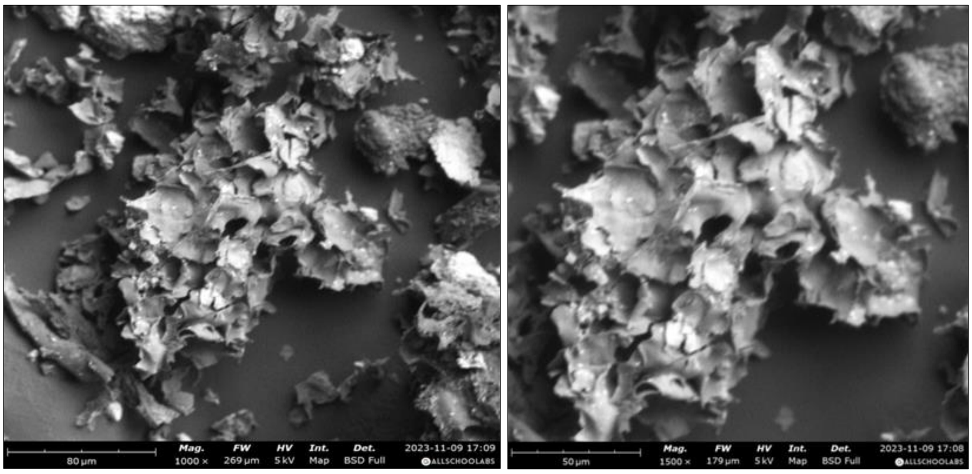

Figure 2c and d: depicts the SEM spectrum for nano composite of *Spondias mombin* fruit before and after adsorbtion

The FTIR spectrum of raw *spondias mombin* seed before and after adsorption displayed in Figure 2 below shows the following:

The FTIR analysis of the raw adsorbent indicates the presence of various functional groups, including C-N, C-O, C-C, N-H, -C≡C and –C≡C-H.

The FT-IR absorption bands at 1027.94cm-1 and 12200cm-^{1} stretches at C-N aliphatic amines group and C-O stretch absorbed at a wave number of 1316. 82CM-1. The absorption band at wave number 1508.20cm-^{1} stretches at C-C (in ring). Wave number 1621.83cm1 indicates the stretch of N-H bend. The stretches of –C≡C group shows weak absorption band at 2020.56cm-2203.41cm-1 and 3291.21 wave number stretches at -C≡ C-H of alkynes (terminal).

These results shows that the adsorption sites offered by these functional groups are responsible for the removal of the studied lead heavy metal through electrostatic attraction or complexation between the metal ions and different *Spondias mombin* fruits.

The FT-IR spectrum of nano composite of *Spondias mombin* fruit before adsorption is displayed in Figure 3 below: The FT-IR analysis of the nano composite adsorbent indicates the presence of various functional groups. C-N, C-O, N-H, C ≡ C, and OH.

The FT-IR absorption band indicates that 1032.59cm^{-1} -1053.49cm^{-1} has C-N stretch, wave band at 1616.67cm^{-1} indicates C-O stretch. The wave band at 1616.67 cm^{-1} has N-H bend stretch, wave bands of 2041.17 cm^{-1} and 2967.25 cm^{-1} has N-H bend stretch while wave bands of 2041.17 cm^{-1} and 2967.25 cm^{-1} shows the presence of -C≡C stretch and 0-H stretch of carboxylic acid, and 3317.71 cm^{-1} wave band indicates that there is N-H stretch.

These results indicate that the presence of these functional groups contributed in the elimination of lead (II) ion from polluted water through electrostatic or complex formation between the adsorbent surface and metal ions.

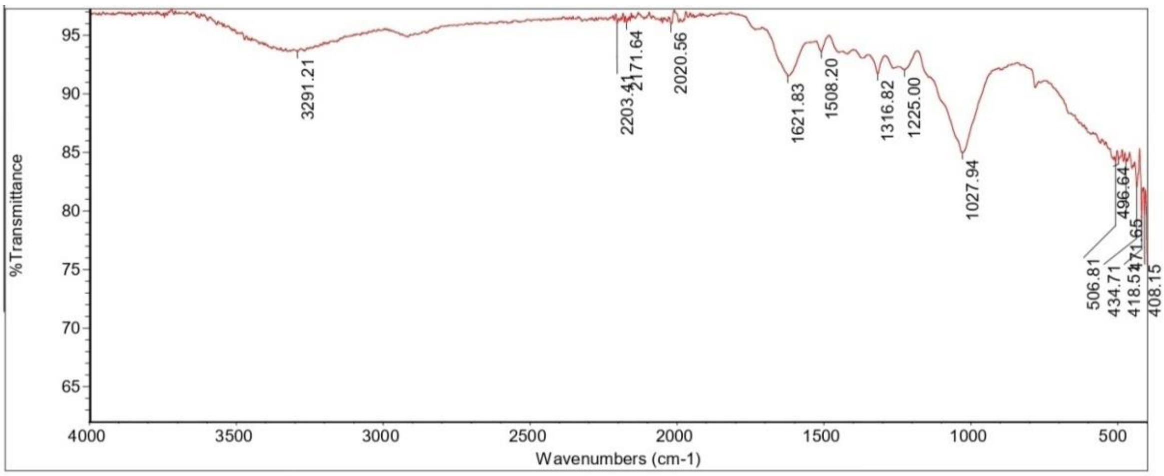

Figure 3: Shows the FT-IR spectrum of raw *Spondias mombin* fruit before adsorption

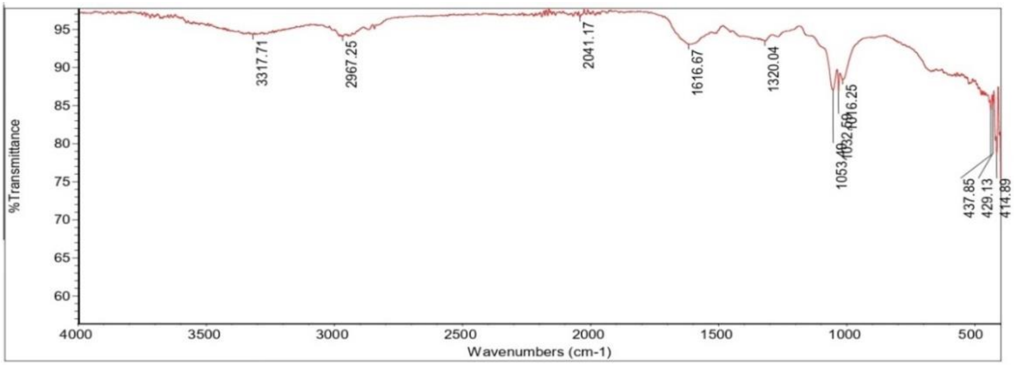

Figure 4: Shows the FT-IR spectrum of nano composite of *Spondias mombin* seed before adsorption

3.2 Adsorption Process Analysis

3.2.1 Effect of Contact Time

The removal of Pb (II) ions was studied under a variable contact time (30, 60, 90, 120 and 180 min) using an optimized amount of 0.2 g of raw and nano composite from *Spondias mombin* fruit and a metal ion concentration of 250 mg/l.

According to the results of percentage removal and adsorption capacity from Figure 5 and 6, it was observed that as the contact time increases, the percentage removal and adsorption capacity increases in the presence of both adsorbent. Equilibrium was attained for lead removal with raw at 60 mins and 150 mins under nano composite adsorbent. Raw adsorbent shows the highest removal efficiency of 78.80 %, while nano composite shows 81.32 %. The close removal efficiency observed shows that both adsorbents have similar characteristics and affinity for the metal ions and their adsorption sites. Furthermore, the raw and nano composite fruit adsorbents showed higher adsorption efficiency for lead (II) ions under the studied adsorbent as observed in this study. This results will draw more attention from researchers in the future for waste water treatment.

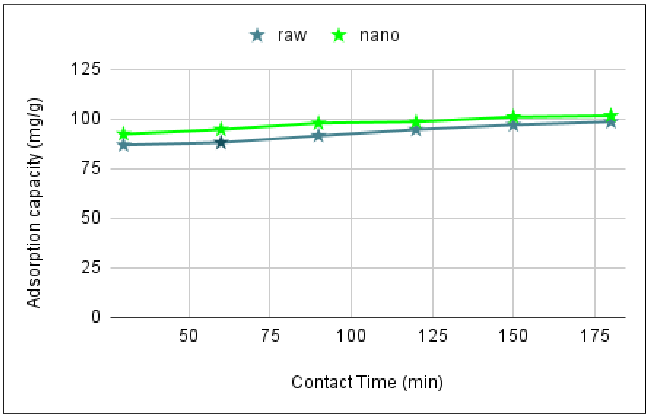

Figure 5: Shows the results of the effect of contact time on the adsorption capacity on the removal of Pb^{2+} ion by raw and nano composite

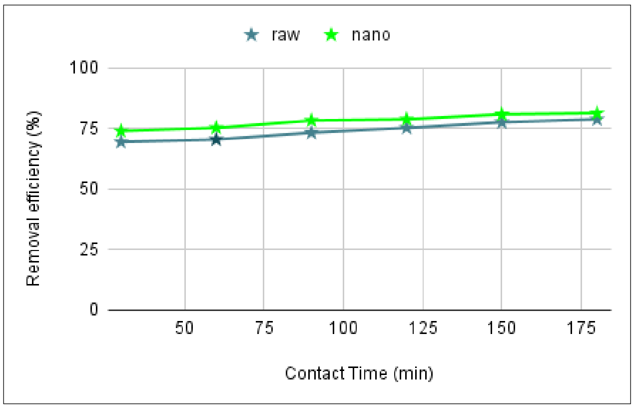

Figure 6: Shows the effect of contact time on the removal efficiency of Pb^{2+} ions by raw fruit and fruit nano composite

3.3 Effect of Adsorbent Dose

In this study, different doses of both adsorbents (0.2, 0.4, 0.6, 0.8, and 1.0g) were applied under lead ion concentration (250 mg/l) and contact time (30 min). The adsorption removal efficiency and adsorption capacity increase of lead ion are shown in Figure 7 and 8, respectively. The experimental findings proved that the removal efficiency increases as the adsorbent dose increase due to a greater availability of surface area at a higher adsorbent concentration. The absorption capacity of both adsorbents decreased with increase in adsorbent dose. The decreasing rate of adsorption capacity obtained in this study may be due to over lapping of adsorbent sites as a result of crowding together of adsorbent particles. It is clear that the adsorbent made from the raw fruit and nano composite showed closed removal efficiency and high adsorption capacity.

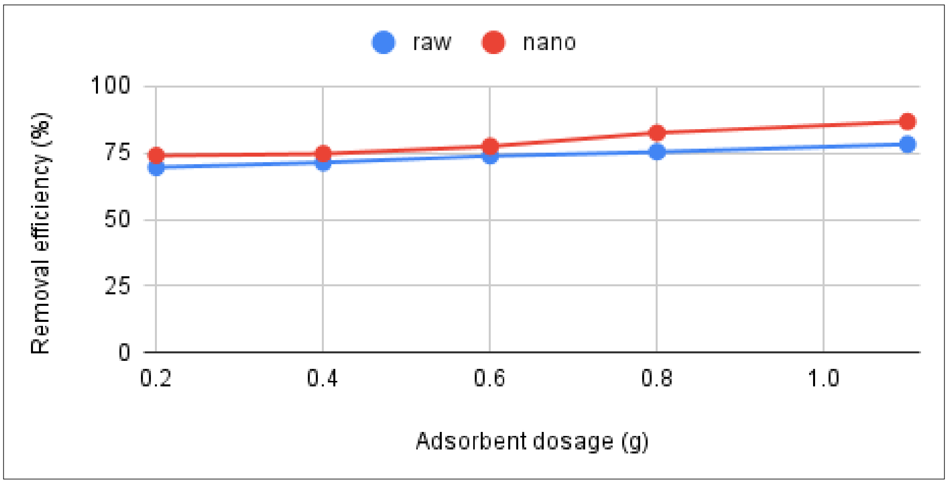

Figure 7: Shows the effect of adsorbent dosage on the removal efficiency of Pb^{2+} ions by raw fruit and fruit nano composite

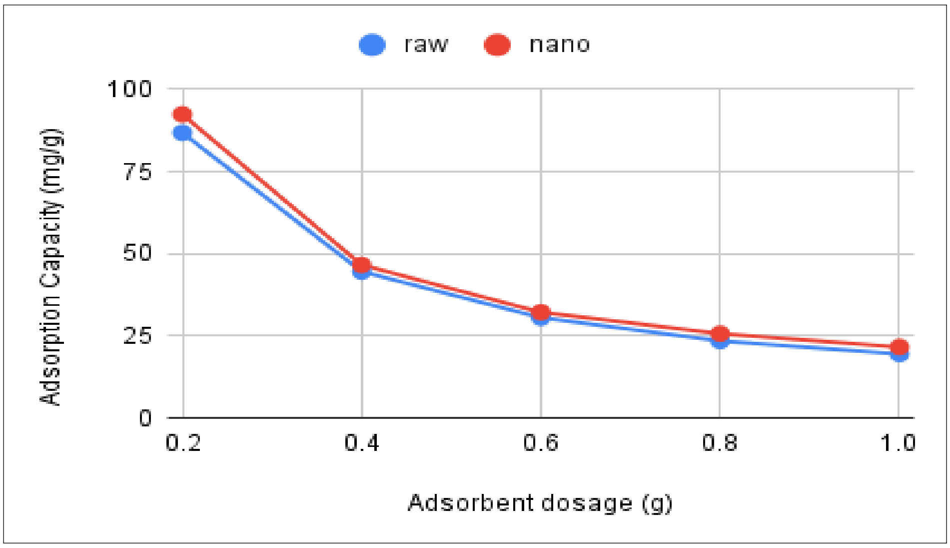

Figure 8: Shows the effect of adsorbent dosage on the adsorption capacity on removal of Pb^{2+} ions by raw and nano composite

3.4 Effect of the Initial Metal Ion Concentration

The effect of the initial concentration on Pb^{2+} ion on percentage removal and adsorption capacity at a constant adsorbent dose of 0.2g / 100ml and a contact time of 30 min are shown in Figures 9 and 10 respectively. The studies were carried out at various adsorption process of Pb^{2+} ions (100, 150, 200, 250, and 300 mg/l). The results obtained showed that the percentage removal decrease with an increase in metal ion concentration. This occurred because Pb ions were quickly adhered to the adsorbent sites at lower concentrations of metal with a larger binding site. The high increase in Pb ion adsorption at the lower concentration can be attributed to the larger binding site of the adsorbent at the earlier time.

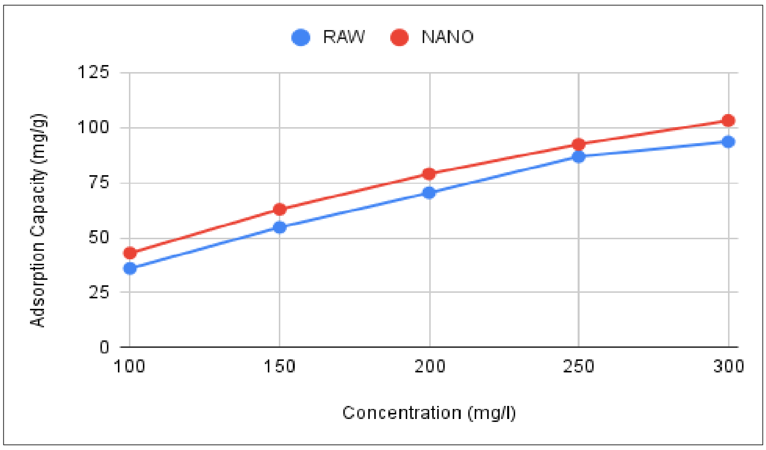

Figure 9: Shows the effect of initial concentration on adsorption capacity on removal of Pb^{2+} ions by raw fruit and fruit nano composite

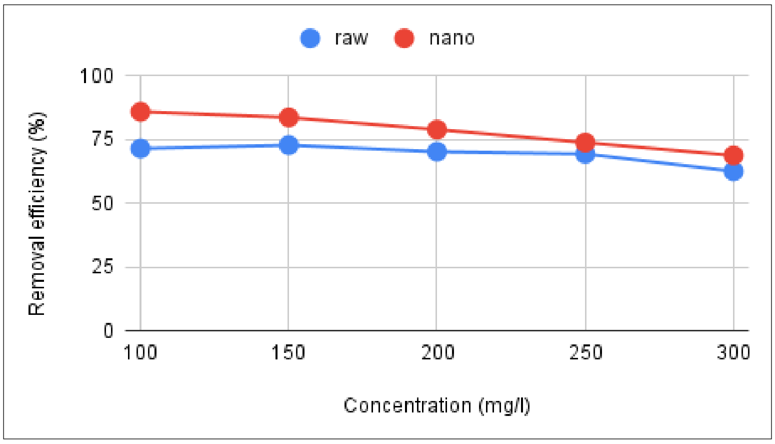

Figure 10: Shows the Effect of initial concentration on the removal efficiency of Pb^{2+} ions by raw fruit and fruit nano composite

3.5 Effect of Temperature

The temperature has a great effect on the adsorption behavior of metal ions in solution, as an increase in temperature affects the adsorbent and absorbent sites and creat a larger surface area for adsorption. This phenomenon either results in a decreased or an increase in the amount of metal ions adsorbed (Nleonu *et al*., 2023). However, Figures 11 and 12 revealed that the rate of percentage removal of Pb^{2+} ions by both adsorbents increases as the solution temperature increases and adsorption capacity also increases with an increase in temperature. The results explained that the strength of intermolecular forces between the adsorbate and absorbent is strongly dependent on the solution temperature and confirmed that the process of Pb^{2+} ion adsorption by both adsorbents were an endothermic process.

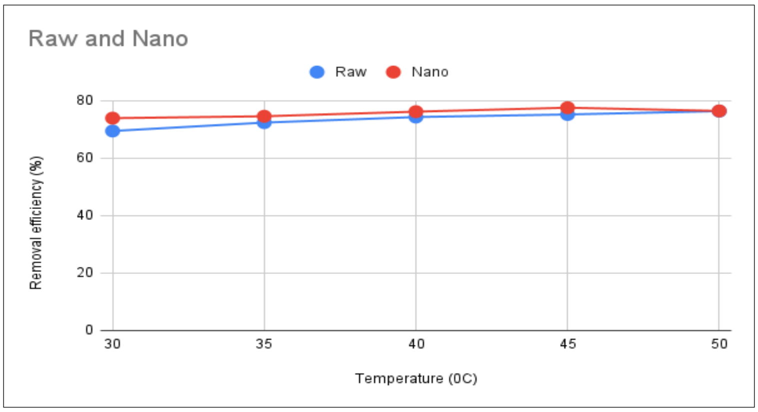

Figure 11: Shows the effect of temperature on the removal efficiency on Pb^{2+} ions by raw fruit and fruit nano composite of *Spondias mombin*

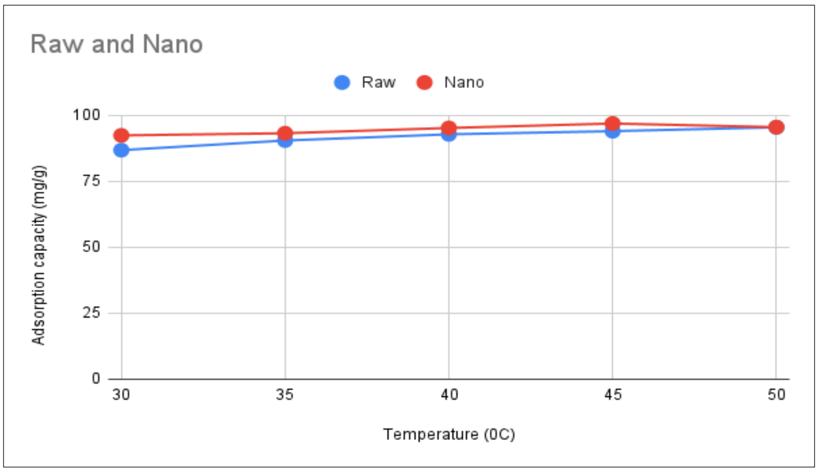

Figure 12: Shows the effect of temperature on the adsorption capacity on the removal of Pb^{2+} ions by raw fruit and fruit nano composite

3.6 Effect of pH

The impact of pH on lead ion adsorption was investigated on five different pH solutions 2, 4, 6, 8 and 10. Figure 13 and 14 revealed that the adsorption rate of Pb^{2+} ions depends on the pH solution. The removal efficiency and adsorption capacity for both raw and nano composite increased as the pH solution increases.The result shows that raw and nano composite fruit of *Spondias mombin* adsorbs more under high pH solution.

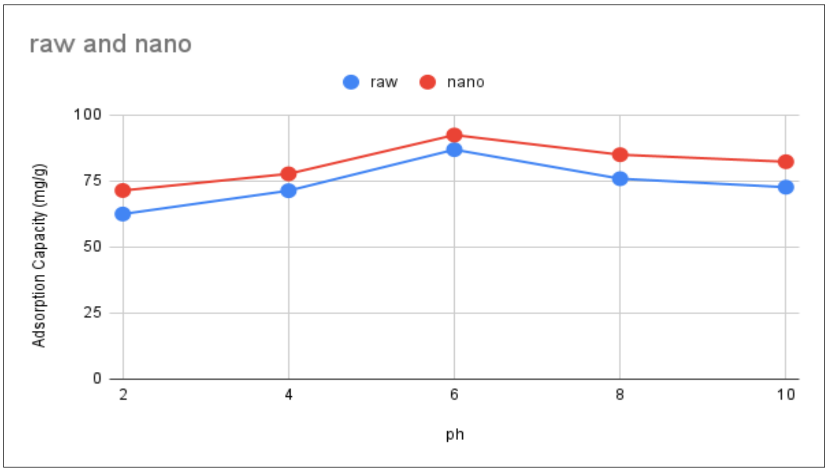

Figure 13: Depicts the effect of pH on the adsorption capacity on removal Pb^{2+} ions by raw fruit and fruit nano composite

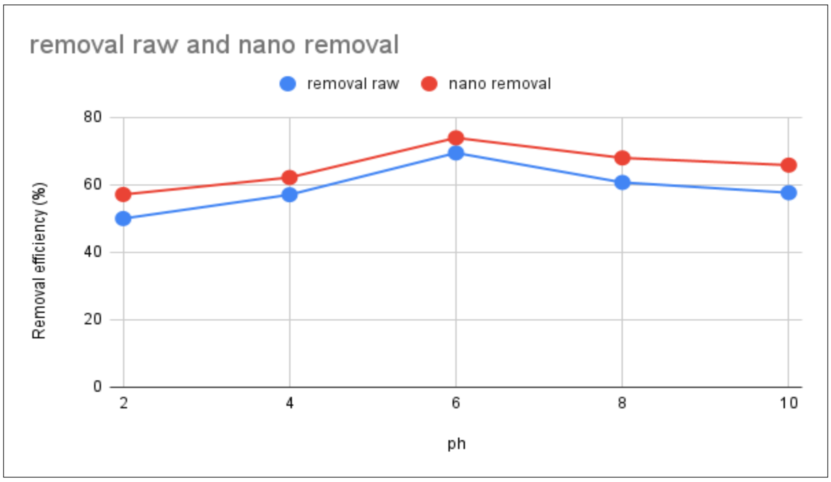

Figure 14: Shows the effect of pH on the removal efficiency on Pb^{2+} ions by raw fruit and fruit nano composite

3.7 Adsorption Kinetic Modeling

The pseudo-first order and pseudo-second order models were fitted to the experimental data in order to estimate the adsorption rate of the adsorbents. The kinetic parameters calculated for the pseudo-first-order and pseudo-second-order models for the adsorbents (raw and nano composite) are shown in Table 1. The experimental results revealed that the linear regression coefficient (R^2) of the pseudo-first-order fitted for the raw sample while the linear regression coefficient (R^2) of the pseudo-second-order fitted for the nano composite. This shows how fast the reaction proceeds between the adsobate and adsorbent in the solution, thereby indicating that raw and nano composite of *Spondias mombin* a reliable and effective adsorbent for wastewater treatment

Table 1: Shows the kinetic adsorption model parameters for Pb^{2+} ion by raw and seed nano composite of *Spondias mombin* on removal of lead (ii) ion.

Adsorbent	Pseudo first order		Pseudo second order	
	K	R^2	K	R^2
Raw seed	0.0028	0.992	2.583×10^{-4}	0.981
Nano composite	0.0023	0.967	4.2×10^{-5}	0.975

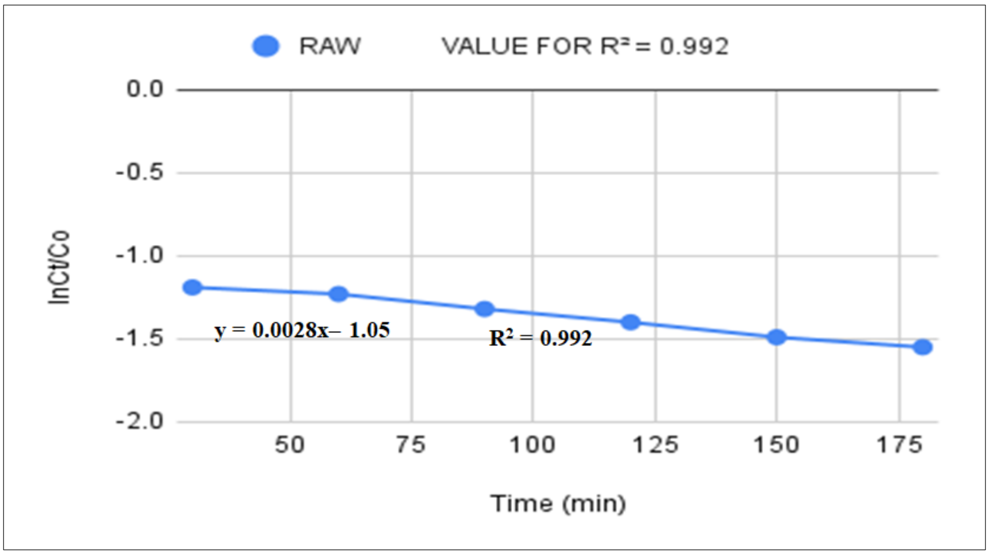

Figure 15: Shows the Pseudo-first-order on the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

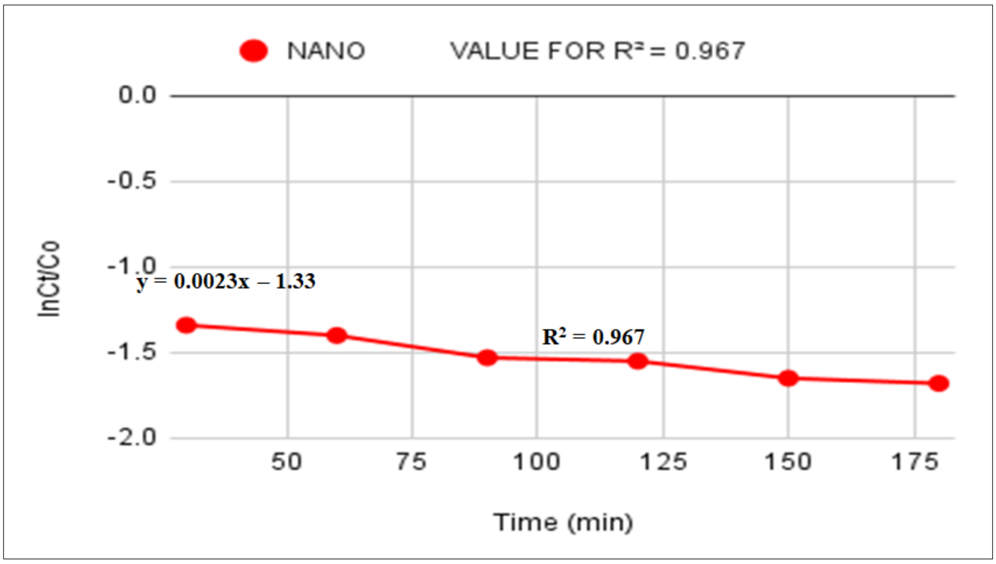

Figure 16: Shows the Pseudo-first-order on the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

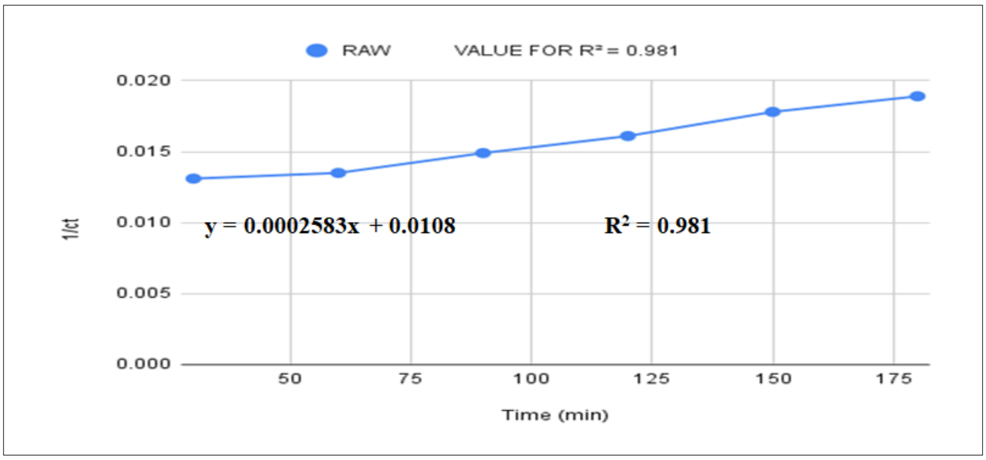

Figure 17: Shows Pseudo-second-order of the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

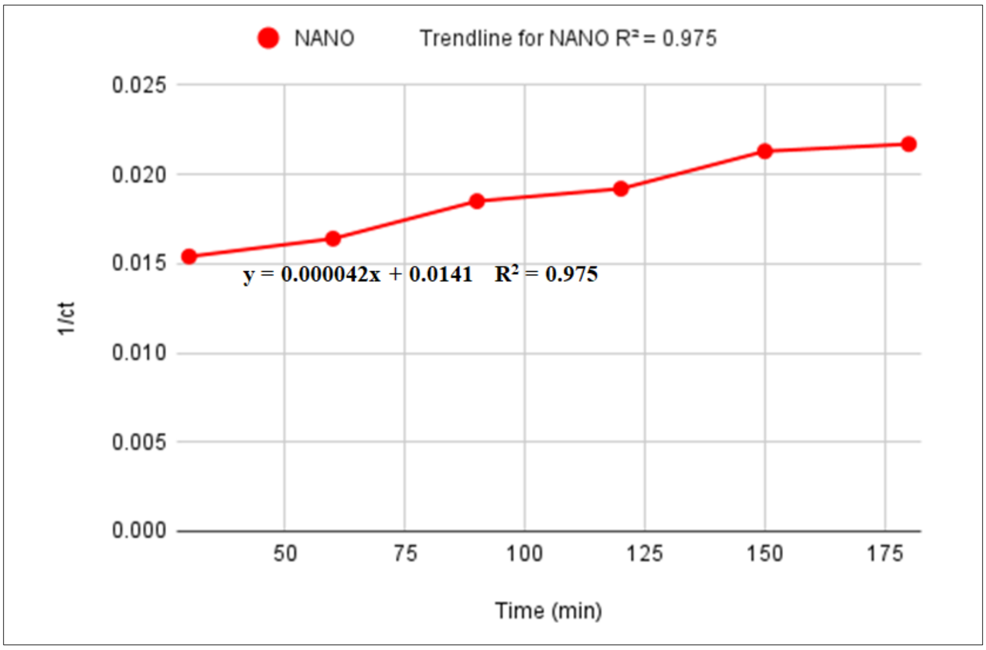

Figure 18: Shows Pseudo-second-order of the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

3.8 Adsorption Isotherm Studies

The adsorption isotherms of the study on removal of lead (II) ion by *Spondias mombin* (raw and nano composite) were explained using the Langmuir and Freundlich isotherm models. The computed Langmuir and Freundlich isotherm parameters are shown in the Table 2 below, along with their correlation coefficients for the adsorption experimental data. The experimental data shows that Langmuir isotherm was well fitted to both adsorbents for Pb^{2+} adsorption based on the R^2 values, which reveals that the adsorption is monolayer and the adsorption surface is homogeneous. From the table below, nano composite of *Spondias mombin* shows larger adsorption capacity (k_l) than the raw seed indicating a strong binding strength on the adsorption surface.

Table 2: Shows the adsorption Isotherm model parameters for the removal lead (II) ion by raw and nano composite of *Spondias mombin* seed

Adsorbent	Freundlich model			Langmuir model		
	n	K_f (mg/g)	R^2	q_L	K_L(mg/g)	R^2
Raw seed	1.14	3.5966	0.94	5.5066	15.1403	0.972
Nano composite	1.89	5.0028	0.974	3.9216	254.7122	0.997

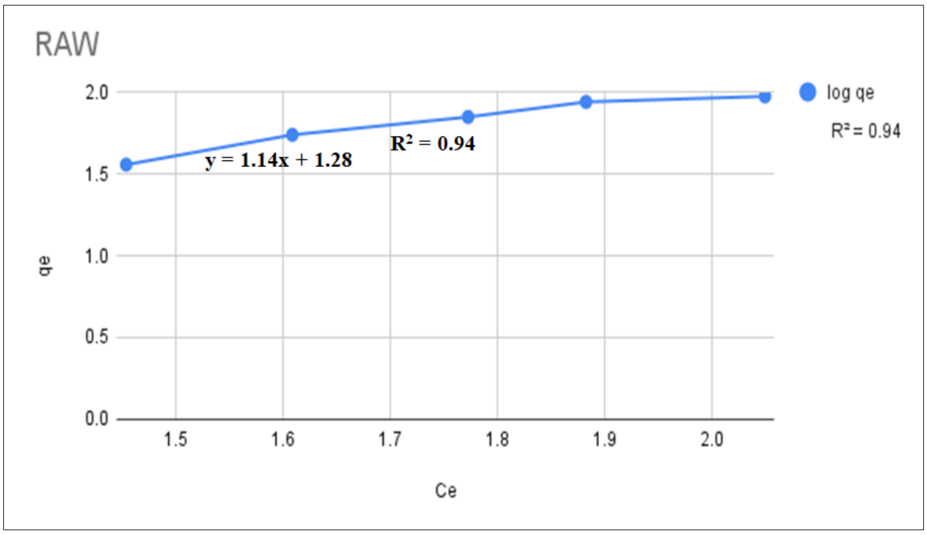

Figure 19: Shows Freundlich adsorption model of the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

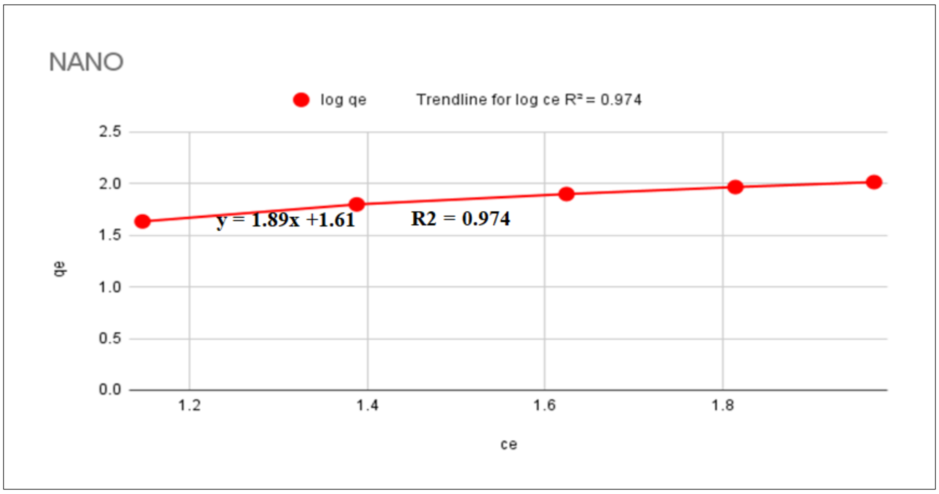

Figure 20: Shows Freundlich adsorption model of the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

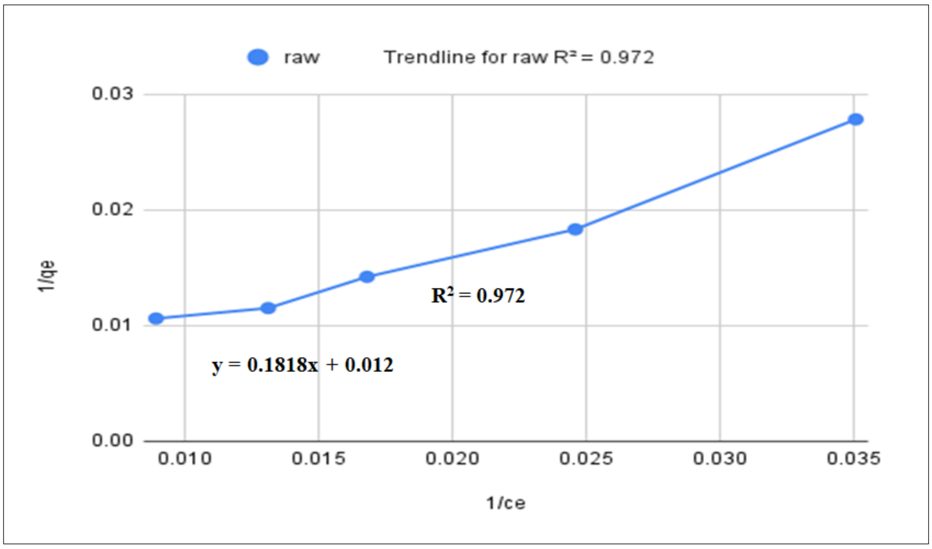

Figure 20: Shows Langmuir adsorption model for the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

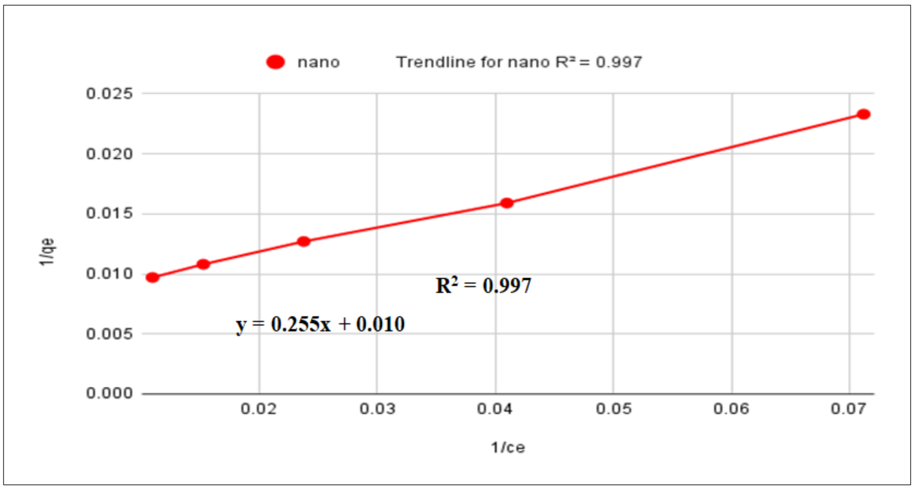

Figure 21: Shows Langmuir adsorption model for the removal of Pb^{2+} by raw and nano composite of *Spondias mombin*

3.9 Thermodynamics Studies

The thermodynamic parameters are important for determination of feasibility, nature of heat adsorption, and spontaneity of the adsorption process. The thermodynamic parameters obtained in this study are presented in table 3, the standard (ΔS^0) was found to be positive for raw and nano fruit for the temperatures tested, and the negative value of (ΔH^0) observed for both raw and nano fruit indicated the adsorption of Pb^{2+} ions by the adsorbent is exothermic. The Gibbs free energy demonstrated the spontaneity of the adsorption processes, and the negative value of (ΔG^0) illustrate that the adsorption of Pb^{2+} ion by both adsorbents were spontaneous. The value of (ΔG^0) was observed to decrease as the solution temperature increased. The study shows that Pb^{2+} ion adsorption was lower at high solution temperature.

Table 3: Shows the thermodynamic parameters on removal of lead (ii) ion by raw and nano composite of *Spondias mombin* seed

Adsorbent	**ΔG^0 (kj/mol)**					**ΔH^0 (kj/mol)**	**ΔS^0 (kj/mol)**
	303 (k)	**308 (k)**	**313 (k)**	**318 (k)**	**323 (k)**		
Raw seed	-3234	-3287	-3341	-3394	-3448	-3.11	1.70
Nano composite	-4068	-4135	-4202	-4269	-4337	-3.99	1.35

4.0 CONCLUSION

However, the efficiency of the raw and nano composite of *Spondias mombin* fruit on the removal of lead (II) ion from aqueous solutions as well as the impact of different variables were investigated. The study showed that the raw and modified adsorbents can be considered effective adsorbent for the removal of lead metal ions from wastewater by varying some basic parameters. The physiochemical properties of the absorbents were analyzed and the results obtained confirmed the adsorption potentials of the raw and nano composite. The removal efficiencies of both adsorbents on the Pb^{2+} ion were strongly dependant on their contact time, initial metal ion concentration, absorbent dosage, pH and temperature. The Langmuir isotherm model was well fitted to the experimental data, indicating that the two absorbents were effective in removing Pb^{2+} ions from aqueous solutions with low absorption energy.

The experimental data of Pb^{2+} ions adsorption by raw and nano composite adsorbents studied were fitted with the pseudo-first-order and pseudo-second-order kinetic model respectively, revealing that adsorption occurs by chemisorptions and physosorption techniques. The thermodynamic data showed that the adsorption process was exothermic, spontaneous and feasible in nature. Therefore, this work exposed the possible removal of lead (II) ion by raw and nano composite from agro waste of *Spondias mombin* from wastewater, which is generally a low cost agro waste.

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