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Equilibrium, Kinetic, and Thermodynamic Studies of Pb (II) ions Adsorption onto Modified Tamarind Fruit Pulp

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Abstract The challenge of accessing clean drinking water in urban Kenya is compounded by contamination from heavy metals, leading to serious health risks such as kidney and brain damage. Industrialization and technological advancement have exacerbated the problem of increase of Pb (II) ions and other heavy metals in water ecosystem through industrial effluents. This study investigated the use of modified tamarind fruit pulp (MTFP) for the adsorption of (Pb II) ions from synthetic wastewater. Characterization techniques like XRF and FT-IR were utilized, and adsorption experiments were conducted by varying pH, contact time, temperature, dosage, and initial concentrations of the metals. The results were analysed statistically using ANOVA, with significant differences at $P \leq 0.05$. The equilibrium studies indicated that the adsorption of Pb (II) ions was best represented by the Freundlich model, with adsorption capacities of 1.30 and 1.67 mg/g for unmodified tamarind fruit pulp (UTFP) and modified tamarind fruit pulp (MTFP), respectively. Thermodynamic study showed that the adsorption process was thermodynamically spontaneous and endothermic. Kinetic studies revealed that chemisorption was the rate limiting step in the adsorption of Pb (II) ions. This information revealed the enhanced capabilities of MTFP to effectively remove Pb (II) ions from wastewater, showcasing its potential as an eco-friendly adsorbent.

Keywords Adsorption, Equilibrium, Kinetics, Tamarind fruit pulp, Thermodynamics

1. Introduction

The pervasiveness of heavy metals in wastewater has risen concurrently with the increase of industrial and human activities. Lead is a fundamental component in many important manufacturing industries, such as the battery and paint industries. These industries discharge effluents with a high amount of Pb (II) ions into the water ecosystem. These non-biodegradable metals have potential carcinogenic properties, highlighting the risk of critical health issues when present in water at high concentrations [1]. Traditional wastewater treatment methods like biological (activated sludge), chemical (coagulation), and physical (filtration) effectively remove pollutants but present challenges such as high costs, land requirements, and difficulties in managing emerging contaminants [2]. Concerns over heavy metal contamination have prompted exploration of eco-friendly solutions, such as using tamarind fruit pulp for the remediation of cadmium and lead in wastewater, which shows promise in effectively adsorbing these contaminants while being cost-efficient and environmentally friendly.

2. Materials and Methods

2.1. Chemical and Reagents

The sodium hydroxide and Hydrochloric acid used in modification of the tamarind fruit pulp and adjustment of pH while lead (II) nitrate was used in batch adsorption studies. The reagents were of analytical grade.

2.2. Modification of Tamarind Fruit Pulp

The tamarind fruit pulp was cleaned thoroughly with distilled water, then dried in an oven at a temperature of 60 ℃ for 24 hours. After drying, the pulps were then grounded into a powder and stored. 170 mL of 3.5 M NaOH was measured and placed in a 250 mL Erlenmeyer flask. 25 g of powdered dried tamarind fruit pulp was weighed and added to the content in the Erlenmeyer flask, and the mixture was placed in a Teflon autoclave at 100 ℃ for 24 hours. The mixture was then filtered, and the residue was washed with distilled water until a pH of 10 in the filtrate was achieved. Then, it was oven-dried at about 60 ℃ and coded as (MTFP) for characterization and adsorption application.

2.3. Characterization of the Adsorbents

The characterization of adsorbents is a crucial initial step in adsorption studies, connecting material structure to

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performance. This process explores retention mechanisms, particularly the interaction between adsorbent surfaces and target pollutants, by assessing key physical and chemical properties. The XRF was used for chemical composition analysis while the FT-IR was used to assess the functional groups present in both the unmodified and modified tamarind fruit pulp.

2.4. Preparation of Pb (II) Ions Sorbates for Adsorption Studies

Stock solutions for adsorption studies were prepared using lead (II) nitrate, which was of analytical grade. Lead (II) ions solution was prepared by dissolving an accurate quantity of 1.559 g of lead (II) nitrate in 600 mL of distilled water and diluting to 1000 mL [3]. The solution was coded as 1000 ppm of Pb (II) ions. The stock solutions were serially diluted to yield working solutions.

2.5. Batch Experiments

Batch adsorption experiments are key laboratory methods used to evaluate an adsorbent's efficiency in removing pollutants like heavy metals, dyes, or pharmaceuticals from wastewater. The process entails mixing a set volume of the adsorbate solution with a specific quantity of adsorbent, followed by agitation until equilibrium is achieved. The effects of various parameters on adsorption of Pb (II) ions from synthetic wastewater using unmodified and modified tamarind fruit pulp were evaluated.

2.5.1. Effect of pH on Adsorption of Pb (II) Ions

The batch experiments involved varying the pH from 2 to 6 to study the adsorption of Pb (II) ions. Solutions of 100 mg/L concentration were placed in stoppered bottles, with unmodified and modified tamarind fruit pulp added. The mixtures were shaken at 120 rpm for one hour at room temperature, then filtered. The residual metal ion concentrations were analyzed using AAS, and mean values were computed.

2.5.2. Effect of Initial Concentration on Adsorption of Pb (II) Ions

The study explored the adsorption of Pb (II) ions on modified and unmodified tamarind fruit pulp, adapting methods from Maingi *et al*. [4]. Initial metal ion concentrations ranged from 20 to 200 mg/L. A precise 0.10 g of the adsorbent was added to 100 mL bottles, followed by 50 mL of metal ion solutions. The mixtures were shaken at 120 rpm for one hour, with three replicates for accuracy. After filtering, the supernatant metal ions were analyzed using AAS.

2.5.3. Effect of Adsorbent Dose on Adsorption of Pb (II) Ions

The effect of adsorbent dose was carried by varying the adsorbent dose. 50 mL of 100 mg/L of metal ion solutions was put in stoppered bottles containing varying doses (0.1- 0.5g) of unmodified and modified tamarind fruit pulp samples. The suspensions were then shaken at room temperature using an electric shaker that was programmed to operate for an hour at 120 rpm. Prior to analysis, each sample was filtered to minimize the impact of the adsorbent particles on the assay [5].

2.5.4. Effect of Contact Time on Adsorption of Pb (II) Ions

The effect of contact time was investigated by varying time from 10 to 100 minutes. In each of a series of adsorption bottles, 0.10 g of the adsorbents UTFP and MTFP were placed. 50 mL of 100 mg/L metal ion solutions was then added to each bottle. The mixtures were shaken using a thermostatic electric shaker set to run at 120 rpm at room temperature. The mixtures were removed from the shaker based on their coded contact time. The mixtures were filtered and residual metal ion concentration determined using AAS.

2.5.5. Effect of Temperature on Adsorption of Pb (II) Ions

The equilibrium temperature for the adsorption of Pb (II) ions was evaluated using the temperature range of 293 K to 328 K. 50 mL of the known concentration of aqueous solution at an ideal pH of 5.0 was added to stoppered plastic bottles containing 0.10 g of the adsorbent for every experimental run. The bottles were put in a thermostatic electric shaker set to a specific temperature and shaken continuously at 120 rpm for an hour. After filtering, the remaining metal ions in the filtrate were examined.

2.6. Adsorption Isotherms

Adsorption data of Pb (II) ions were fitted in both Freundlich and Langmuir isotherms to assess the adsorption capacities of UTFP and MTFP [6]. The residual metal ion concentrations were analysed using AAS, with the equilibrium adsorption (q_e) amount calculated using Equation 1 [7].

$$q_e = \left[\frac{C_0 - C_e}{W}\right]\mathrm{V} \quad (1)$$

where C_o and C_e (mg/L) represent the initial and equilibrium concentrations of the corresponding metal ions, respectively. W (g) is the mass of the dry adsorbent employed, and V is the volume of the solution used (L). Equation 2 shows the linearized Freundlich isotherm used in this study.

$$lnq_e = lnK_F + \frac{1}{n}lnC_e \quad (2)$$

Where: K_F= Freundlich isotherm constant associated with adsorption capacity, q_e = adsorption at equilibrium, 1/n= Heterogeneity index associated with adsorption intensity, C_e = concentration of the adsorbate in solution at equilibrium. Equation 3 shows the linearized Langmuir adsorption isotherm [4].

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

Where, C_e is the concentration of metal ions at equilibrium (mg/dm^3); q_e is the amount of Pb (II) ions adsorbed (mg/g); q_m is the adsorption capacities (mg/g);

K_L is the isotherm constant (dm^3 /mg).

2.7. Thermodynamic Study of Adsorption of Pb (II) Ions

The study investigated the effect of temperature on thermodynamic parameters using batch experiments across a range of temperatures: 20, 30, 40, 50, and 55 ℃. Each experiment involved combining 0.2 g of adsorbent with 50 mL of 100 mg/L metal ion solutions at solution pH 4.0. After one hour, the mixture was filtered, and the residual metal ions concentration in the filtrate analyzed using AAS. The standard entropy and enthalpy changes were calculated using Equations 4 and 5 respectively.

$$\Delta G^{\circ} = -RT\ln K \tag{4}$$

$$\ln K = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/RT) \tag{5}$$

Where R is the gas constant, K is the Langmuir constant and T is the absolute temperature [4].

2.8. Kinetic Studies

The influence of time on sorption was used to analysed the kinetic behaviour of sorbates on adsorbents. Pseudo-first order and Pseudo-second order were used to study the transient behaviour of the adsorption process. Equation 6 was used in calculating of q_t.

$$q_t = \frac{(c_0 - c_t)}{w} \times V \tag{6}$$

Equations 7 and 8 represents the linearized Pseudo-first and Pseudo-second order equations respectively. Plotting graphs of log $(q_e - q_t)$ against t for pseudo-first order and t/q_t against t for Pseudo-second order using the collected data allowed for the determination of kinetic parameters using Equations 7 and 8, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{K_t}{2.303} \tag{7}$$

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

Where: V is the volume of adsorbate solution in L and W is the mass of the adsorbent in g. q_e is the amount adsorbed at equilibrium, q_t is the amount absorbed at any given time, t is the time in minutes, K is the Lagergren rate constant and K_2 is rate constant for pseudo second order [4].

3. Results and Discussions

3.1. XRF Analysis of the Adsorbents

The X-ray Fluorescence spectrometer (model S1 Titan) was used to determine the chemical composition of the Tamarind fruit pulp and modified tamarind fruit pulp. Table 1 shows chemical composition of both the modified and unmodified Tamarind fruit pulp.

The MTFP and UTFP primarily consist of silica (SiO_2) and alumina (Al_2O_3), with mean percentages of 91.691 ±0.224 and 53.369 ±0.128, respectively. Silica's higher percentage is crucial for the fruit's rigidity and toughness, as the tamarind tree extracts minerals and silicon from poor soil conditions. Modification increases SiO_2 levels due to reactions with an alkaline activator. Other elements include magnesium oxide (MgO) at 11.622% for UTFP and 1.990% for MTFP, along with various oxides and minerals such as aluminum oxide (Al_2O_3), phosphorus (P), sulphur (S), calcium (Ca), and iron (Fe). This mineral absorption is reflected in the fruit pulp, which also contains phytochemicals that contribute to the formation of these oxides.

Table 1. Mean percentage chemical composition of unmodified tamarind fruit pulp (UTFP) and modified tamarind fruit pulp (MTFP)

Element/oxide	UTFP Mean %±SD	MTFP Mean %±SD
MgO	11.622 ±0.446	1.190 ±0.416
Al_2O_3	3.515 ±0.101	0.917 ±0.100
SiO_2	53.369 ±0.128	91.691 ±0.224
P	1.143 ±0.013	0.306 ±0.013
S	1.361 ±0.013	0.369 ±0.014
Cl	0.636 ±0.014	0.693 ±0.021
K_2O	22.000 ±0.019	0.334 ±0.008
Ca	4.318 ±0.019	2.418 ±0.030
Mn	0.053 ±0.003	0.038 ±0.002
Fe	1.106 ±0.002	0.836 ±0.005

SD- Standard deviation, UTFP-unmodified tamarind fruit pulp, MTFP-modified tamarind fruit pulp.

3.2. FT-IR Analysis of UTFP and MTFP

Fourier Transform Infrared (FT-IR) analysis was performed using a Shimadzu-119 instrument, calibrated after warming for 30 minutes with inactive potassium bromide. About 1mg of each powdered sample was mixed with potassium bromide in a 1:50 ratio, ground for homogeneity, and compressed into a translucent pellet. This pellet was then placed in the FT-IR machine for analysis, and the FT-IR spectrum was generated to interpret various peaks of interest. The spectrum for transmittance against wavelength for UTFP is illustrated in Figure 1.

The FT-IR analysis of the UTFP adsorbent revealed key functional groups, including hydroxyl, carbonyl, amine, and double covalent bonds, with carboxyl and amino groups acting as primary adsorption sites for lead and cadmium. Significant peaks were identified at 3313.97 cm^{-1} (O-H or N-H stretching), 2926.10 cm^{-1} (C-H stretching), 1729.71 cm^{-1} (C=O stretching), and 1408.36 cm^{-1} (C-H bending). Additional peaks at 1304.71 cm^{-1} (C–O stretching), 1257.71 cm^{-1}, 1203.52 cm^{-1} (C-O stretching), 1011.02 cm^{-1} (Si-O and C-O stretching), and 838.36 cm^{-1} (C-H bending) further characterized the molecular structure. Peaks at 784.29 cm^{-1} and 674.49 cm^{-1} indicated out-of-plane C-H bending. These bands are specific for the presence of important phytochemicals viz. polyphenols and flavonoids containing aromatic rings in tamarind fruit pulp. The spectrum was modified using sodium hydroxide. The Figure 2 shows the spectrum obtained upon modification using sodium hydroxide.

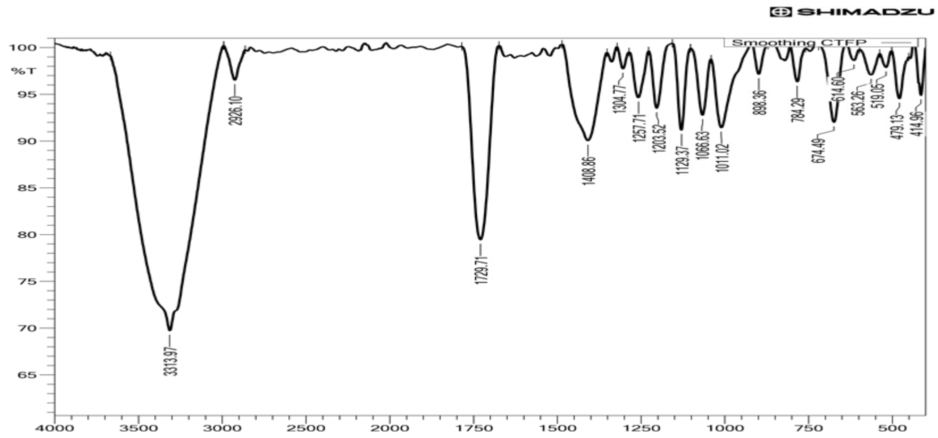

Figure 1. FT-IR spectrum for UTFP

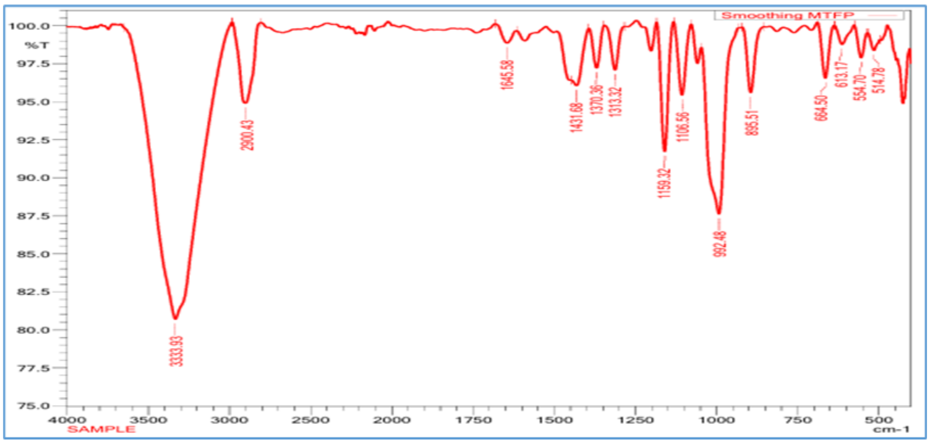

Figure 2. FT-IR spectrum for MTFP

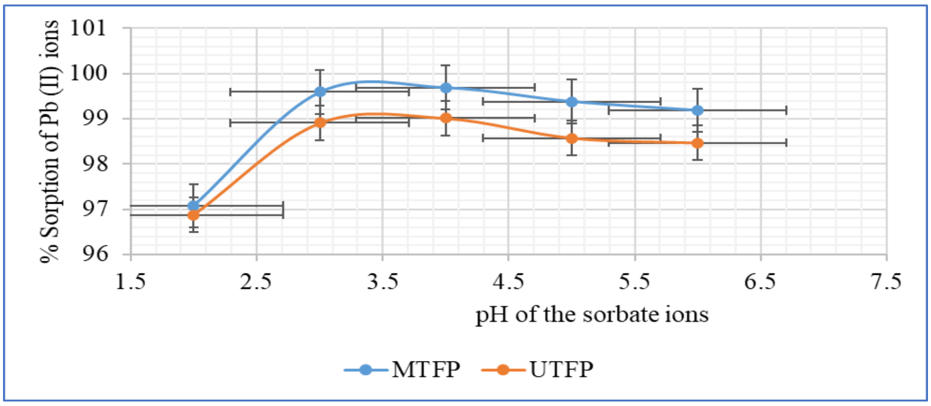

Figure 3. Effect of pH on adsorption of Pb (II) ions on UTFP and MTFP

Upon modification, a blue shift occurred where the peak at 3313.97 cm^{-1} in UTFP shifted to 3333.93 cm^{-1} in MTFP. A red shift was observed when the peak at 2926.10 cm^{-1} shifted to 2900 cm^{-1} upon modification. This could have been contributed to by the fact that -OH added during modification acted as a hydrogen bond donor, elongating the bond and hence weakening it. The peak at 1729.71 cm^{-1} disappeared in MTFP, possibly due to the conversion of COOH groups in tamarind fruit pulp to COO- on addition of an alkali [8]. Additionally, the intensity of the peak at 1408 cm^{-1} decreased, indicating consumption or alteration of the aliphatic C-H or carboxyl groups, while the peak at 1011.02 cm^{-1} increased in intensity due to an elevated O-H concentration from sodium hydroxide incorporation.

3.3. Effect of pH on Adsorption of Pb (II) Ions Using UTFP and MTFP

The batch experiments varied the pH from 2 to 6, with results depicted in Figure 3, showing the adsorption of Pb (II) ions using UTFP and MTFP adsorbents.

The mean percentage removal of Pb (II) ions was improved from 99.011% to 99.687% with the use of UTFP and MTFP, respectively. Optimum adsorption occurred at pH 4.0, as high concentrations of H^+ ions at low pH reduced adsorption efficiency by competing with Pb (II) ions for active sites on the adsorbent. Increasing the pH from 2 to 4 enhanced Pb (II) ion adsorption due to reduced H^+ concentration [5]. However, between pH 5 and 6, removal efficiency declined, attributed to a decrease in the protonation of functional groups on the adsorbent.

3.4. Effect of Initial Concentration on Adsorption of Pb (II) ions

The study examined the impact of initial concentrations of Pb (II) ions on their removal efficiency, using an adsorbent dose of 0.1 g and a stirring rate of 120 rpm. Adsorption was analyzed at initial concentrations of 20, 50, 75, 100, 150, and 200 mg/L, with results illustrated in Figure 4.

The removal percentage of Pb (II) ions using MTFP initially decreased from 98.72% to 97.60% and fairly remained constant when the initial concentration was varied from 20- 200 mg/L. Similarly, removal efficiency using UTFP's dropped from 97.83% to 96.13%. As metal ion concentration rises, the residual sorbate ion in solution increases, leading to reduced adsorption as available sites on the adsorbent get saturated [9]. Lower concentrations permit better adsorption rates due to fewer Pb (II) ions compared to available sites, while higher concentrations occupy most sites, diminishing removal efficiency [10].

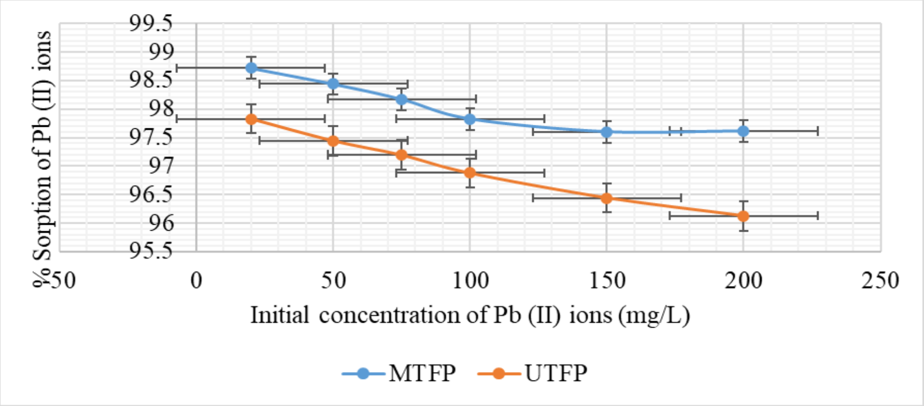

Figure 4. Effect of initial concentration on Pb (II) ions uptake using UTFP and MTFP (Adsorbent dose=0.1g, shaking speed=120rpm, pH=4.0)

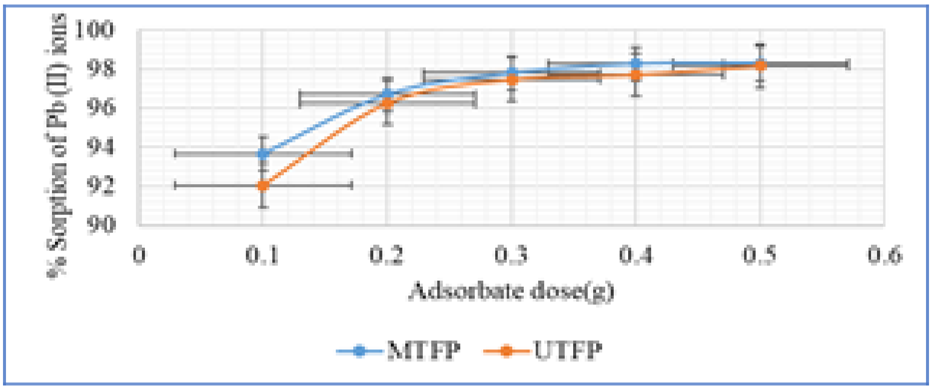

Figure 5. Effect of adsorbent dose on Pb (II) ions uptake using MTFP and UTFP

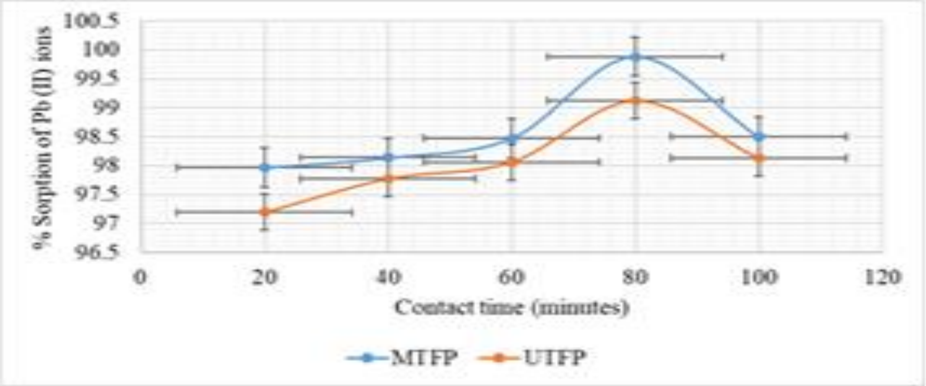

Figure 6. Effect of contact time on Pb (II) ions uptake using MTFP and UTFP (Pb (II) ions

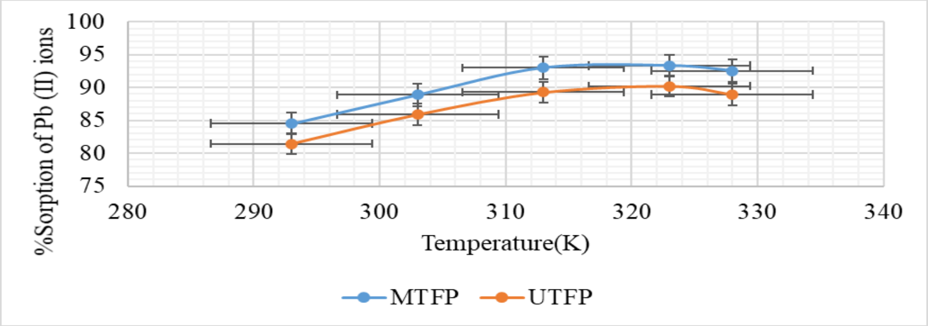

Figure 7. Effect of temperature on Pb (II) ions uptake using MTFP and UTFP

Table 2. Isotherm model constants and correlation coefficients for adsorption of Pb (II) ions on UTFP and MTFP

	Freundlich			Langmuir		
Sorbent	1/n	K_F (mg/g)	R^2	K_L (L/mg)	Q_{max} (mg/g)	R^2
UTFP	0.498	1.30	0.668	-0.013	-0.155	0.420
MTFP	0.232	1.67	0.892	0.032	0.130	0.720

UTFP- Unmodified Tamarind Fruit Pulp, MTFP-Modified tamarind fruit pulp, 1/n = heterogeneity index,
K_F =Freundlich constant, R^2= correlation coefficient, Q_{max}= adsorption capacity, K_L = Langmuir constant.

Table 3. Adsorption thermodynamic parameters of Pb (II) ions

				ΔG^0(kJ/Mole)				
Adsorbents	Metal ions	ΔH^0	ΔS^0	293K	303K	313K	323K	328
UTFP	Pb (II)	7.96	42.87	-4.60	-4.72	-5.40	-6.00	-6.92
MTFP	Pb (II)	5.37	36.04	-5.15	-5.45	--5.73	-6.06	-6.93

UTFP= Unmodified tamarind fruit pulp, MTFP= Modified tamarind fruit pulp, $\Delta H^{0=}$ Standard enthalpy change,
ΔS^0 = Standard entropy changeΔG^0=Standard free energy change

Table 4. Descriptive data on rate constants of Pb (II) ions adsorption onto UTFP and MTFP as estimated from Pseudo- first and second order kinetic models

		Pseudo- first order						Pseudo- second order			
Adsorbent	Ions	q_e(exp)	SD	q_e(Cal)	SD	K_1	R^2	q_e(Cal)	SD	H_0	R^2
UTFP	Pb (II)	28.96	0.06	2.32	0.61	3.981	0.695	29.32	0.20	30.44	0.97
MTFP	Pb (II)	22.97	0.04	2.29	0.44	16.413	0.782	23.12	0.13	67.02	0.92

UTFP=Unmodified tamarind fruit pulp, MTFP= Modified tamarind Fruit pulp, SD=Standard Deviation,
qe(exp)(Mg/g) =qe obtained from adsorption experiments, qe(cal)(Mg/g) =qe calculated from Pseudo graphs.
K_1= rate constant for Pseudo first order reaction, ho=Initial sorption rate, (Mg/gmin), R^2= correlation coefficient.

3.5. The Effect of Adsorbent Dose on Adsorption Process

The study investigated the removal efficiency of Pb (II) ions at various adsorbent doses under a shaking speed of 120 rpm, an initial concentration of 100 mg/L, and a pH of 4.0. Results are illustrated in Figure 5, highlighting the impact of adsorbent dose on the adsorption of Pb (II) ions.

The results indicate an increase in Pb (II) ion uptake with adsorbent dose increasing from 0.1 g to 0.5 g. The mean percentage removal increased from 92.04% to 98.18% for UTFP and from 93.67% to 98.27% for MTFP, with an optimal dose of 0.4 g for MTFP. This trend is attributed to the greater availability of active sites and increased surface area of the adsorbents, leading to exponential growth in Pb (II) removal as dosages rise [11].

3.6. The Effect of Contact Time on Adsorption

The study highlights the importance of determining the optimal time for the complete removal of target metal ions and characterizing the speed of heavy metal ion binding by UTFP and MTFP adsorbents. It specifically examines the effect of contact time on the percentage removal of Pb (II) ions at a starting concentration of 100 mg/L, using an adsorbent dose of 0.1 g/50 mL and a shaking speed of 120 rpm, with results illustrated in Figures 6.

The adsorption of Pb (II) ions improved from 97.19% to 99.12% with UTFP and from 97.97% to 99.89% with MTFP, peaking at 80 minutes for both adsorbents. MTFP demonstrated the highest removal efficiency, likely due to more active sites from surface modification. Adsorption rates increased gradually, but not linearly, and peaked between 20-80 minutes before declining. This decline is linked to the dynamic balance of adsorption and desorption as vacant sites become occupied, reversing concentration gradients and releasing previously bound ions [12].

3.7. The Effect of Temperature

In adsorption reactions, temperature significantly affects adsorbate mobility and metal ion absorption into pores, enhancing adsorption rates. Higher temperatures alter adsorbate solubility and chemical interactions between the sorbate and the sorbent. This phenomenon is because an increase in temperature increases kinetic energy and shifts thermodynamic equilibriums, impacting the overall adsorption rate, as observed in the study of Pb (II) ion removal using UTFP and MTFP. Figure 7 illustrates the results obtained when temperature was varied from 293 to 328K.

The mean percent removal increased from 81.42% to 90.22% and 84.51% to 93.33% when UTFP and MTFP were used, respectively. The increment in adsorption with an increase in temperature could be likely attributed to increased ion mobility, thus increasing the number of ions that interact with active sites on the adsorbent surfaces [13]. A slight decline in percentage removal was recorded after 323K for both adsorbents. This could be attributed to the fact that at high temperatures, the physical forces, such as Vander Waals forces, weaken, leading to desorption of trapped Pb (II) ions leading to lowering the removal efficiency. The influence of temperature on the adsorption process is crucial, particularly for determining whether it is endothermic or exothermic. The trend shown in the Figure 7 clearly indicates that the adsorption of Pb (II) ions onto both UTFP and MTFP was a chemisorption. This is because in chemisorption adsorption increases initially as temperature rises and then decrease at much higher temperatures as the exothermic nature of the process starts to favour desorption.

3.8. Adsorption Isotherms

The adsorption data for Pb (II) ions on UTFP and MTFP adsorbents were analyzed using Langmuir and Freundlich isotherms, as detailed in Table 2, which presents the parameters for both isotherms.

From Table 2, the values of (1/n) for both UTFP and MTFP were below one, indicating a highly heterogeneous adsorption surface and favorable adsorption. The MTFP showed a better fit for experimental data compared to UTFP (R^2). Surface modification increased adsorption capacity from 1.30 to 1.67 mg/g. The correlation coefficients for both models (UTFP and MTFP) in the adsorption of Pb (II) ions were lower under the Langmuir model than those in the Freundlich model, which provided a better fit for the data. Consequently, the Freundlich isotherm was used to determine the adsorption capacity of Pb (II) ions for both adsorbents.

3.9. Thermodynamics Studies of Adsorption of Pb (II) Ions onto UTFP and MTFP Adsorbents

The thermodynamic parameters for the adsorption of Pb (II)ions onto modified Tamarind fruit pulp adsorbents at various temperatures are outlined in Table 3.

The changes in free energy ($\Delta G°$) were negative for all adsorbents across various temperatures, indicating a spontaneous process. Higher temperatures enhance the spontaneity of adsorption, with decreasing ΔG values suggesting that the reaction becomes more favorable. Positive entropy changes values indicate significant structural changes at the adsorbents' active sites during the adsorption process, as metal ions must shed part of their hydration sheath [14].

3.10. Kinetic Modeling for Adsorption of Pb (II) Ions

The pseudo-first and pseudo-second order kinetic parameters calculated by linear regression for Pb (II) ions are summarized in Table 4.

The data aligns closely with a pseudo-second order kinetics model, indicated by R^2 values of 0.97 and 0.92 for adsorbents UTFP and MTFP. The initial adsorption rates for Pb (II) ions were 30.44 to 67.02 mg/g min for UTFP and MTFP respectively. The first order rate constant k_1 and equilibrium adsorption density q_e were calculated but showed significant deviation from experimental values. However, the second order kinetic model's q_e values matched well with experimental data, confirming that the adsorption of Pb (II) ions occurred through chemical processes. This suggests that chemisorption is the primary mechanism in the rate-controlling step, as similarly observed in tea waste's adsorption of copper and lead [15].

4. Conclusions

The FT-IR study showed that modification occurred. A blue shift of the peak at 3313.97 in UTFP to 3333.93 cm^{-1} in MTFP, after modification. This shows clearly that -OH was anchored on the surface of tamarind fruit pulp. Also, the red shift observed at the peak at 2926.10 cm^{-1} in UTFP spectrum to 2900 cm^{-1} in MTFP is an indicator of increased -OH on the surface of tamarind fruit pulp. The adsorption of Pb (II) ions onto the adsorbents were influenced by the parameters studied i.e., pH, adsorbent dose, contact time, initial metal ion concentration, and temperature. The mean percentage removal of Pb (II) ions were higher in MTFP than in UTFP clearly indicating that modification enhanced the heavy metal ions uptake. The adsorption data fitted best in Freundlich isotherm indicating that the adsorption process occurred on a heterogenous surface. The thermodynamic studies showed that the adsorption process was spontaneous. Chemisorption was the rate-limiting step in the adsorption of Pb (II) ions, according to kinetic studies.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could appear to have influenced the work described in this paper.

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