Adsorption Studies of Pb^{2+} From Aqueous Solutions Using Unmodified and Citric Acid – Modified Plantain *(Musa paradisiaca)* Peels

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Abstract: *The adsorption of Pb^{2+} from simulated aqueous solution with ground plantain peel biomass and the citric-acid-modified form was studied in a batch adsorption system. The adsorption was strongly pH and temperature-dependent as maximum adsorption was recorded at a pH of 5 and temperatures of 328 K (for unmodified biomass) and 318 K (for modified biomass). The kinetics of both adsorption processes was best fitted by the pseudo-second-order reaction and they were endothermic processes. The unmodified biomass was best fitted by the Langmuir adsorption isotherm while the modified biomass, on the other hand was best fitted by the Freundlich isotherm. Thermodynamic studies revealed an endothermic process for both the modified and unmodified biomass and in addition spontaneity for the former and non-spontaneity for the latter. The maximum adsorption capacity obtained was 49.26 mg/g. Therefore, citric acid – modified ground plantain peel exhibited higher sorption efficiency than the unmodified form for adsorbing Pb^{2+} from simulated aqueous solution.*

Keywords: *Adsorption, citric acid, lead (II), plantain peels, unmodified.*

I. Introduction

The hazardous effects of heavy metals on human and the environment have been of utmost concern in recent years. Their non-biodegradability has raised a lot of issues globally causing the scientific community to seek friendlier and cost-effective approaches for their removal. Ranging from occurrences of carcinogenesis [1] down to genetic mutations, heavy metals have been observed to cause damaging effects due to their high toxicity levels. Sources of these metals include effluents coming from a vast array of industrial plants (paint, metallurgical, plastics, food, etc) and emissions from rickety vehicles [2] and machineries. Lead is one of the most toxic heavy metals that occur naturally in the earth. Several deaths have been recorded in human's history as a result of lead poisoning and it is also known to be one of the propellants of cancer growth. Several methods have been employed for the removal of lead ions; notably adsorption, chemical precipitation, ion-exchange, membrane filtration and reverse osmosis [1, 2, 3]. Due to its versatile nature, high removal efficiency and less-sophisticated design, adsorption is one of the most commonly-used methods that have been employed to reduce levels of lead ions in waste water. Useful adsorbents include activated carbon, bentonite, kaolinite, clay, carbon nanotubes and newly-discovered adsorbents [1] that involve heterogeneous mixtures. The high cost and difficulty of regeneration of most of these adsorbents have led to the search for other low-cost materials that can be easily accessible and sustainable for a long period of time. To further increase the sorption potency of these materials, engineering processes have been carried out to enable them adsorb more metals-one notable example of this is the engineered biochars [4]. Success was also recorded in the use of bio-based ion-imprinted tetraethylenepentamine (TEPA) modified chitosan beads to adsorb lead ions [5]. This modification allowed for the increase in surface area of the adsorbents. Groundnut husk modified with Guar Gum also showed a high potential of remediating lead ions [3]. Other materials that have been used include alginate [6], pectin [7-9], chitin and chitosan [10,11].

Successful results continue to evolve from the use of modified biomass for metal ion adsorption. Yeast biomass modified with ethylene diamine was used for the adsorption of Pb^{2+} in [21]. Results obtained showed an excellent ability of the yeast biomass to adsorb the ions because of the pores that are inherent in it- the presence of the pores were confirmed with the Scanning Electron Microscopy. In [22], Pb^{2+} was adsorbed using diatomaceous earth that was modified with surfactant. The results obtained were consistent with previous studies as modification helped to increase amount of metals sorbed. Other factors that strongly affected the efficiency of adsorption include adsorbent dosage, ionic strength and temperature.

In some other studies, the use of modifiers was neglected. This may be due to the abundant availability of pores and adsorption sites in the biomass. Solid wastes obtained during production of olive oil were used to adsorb Pb^{2+} in [23]. The maximum lead uptake was impressive and FTIR spectra obtained showed that carboxyl groups contributed majorly to the high sorption. The amount of ions adsorbed in [24] which made use of natural sepiolite was much higher than that obtained in [23]. Adsorption amounts, perhaps, would have been higher if

modifiers were employed. The effect of modification was investigated in [4] and it was observed to have increased modification by 2.6 to 5.8 times.

Plantain peel is a potential excellent adsorbent because of its relatively low cost, availability and excellent bio-sorption capacity [12]. It is one of the carbonaceous materials used in the preparation of activated carbon- which is one of the most widely used adsorbents in remediation of heavy metals from waste water. This is attributed to its high sorption capacity, surface area and chemical properties that favour surface-metal bonding [13], [14]. Plantain is readily available in the sub-Saharan region of Africa because it is widely cultivated [15] and the peels are often dispatched as wastes by farmers and households after the fruit have been consumed. It can be consumed in the unripe, partially-unripe and fully-ripped stages [16]. It is common practice in Western Nigeria to feed domestic animals (for example goats) with the peels. The peels account for about 40% of the total weight of the fresh plantain [17] and has lower value to the fruit- which can be consumed directly as foods or processed into chips, flour and beer [18].

Motivated by a number of factors including successes achieved with use of plantain peels as adsorbents for a number of metal ions and the relative abundance of the plantain peel biomass, we sought to investigate the potential of achieving increased sorption of metal ions after chemical modification of biomass. The choice of citric acid was informed by its low cost and biodegradability/environmental friendliness. The choice of lead was influenced by its notoriety for being toxic and the availability of many adsorption studies using the metal. While we are aware that some studies have investigated metal sorption using plantain peels, we are not aware of any work that has undertaken exactly the same study as ours. The study seeks to answer the following questions: Can plantain peels be chemically modified using citric acid? Can citric-modified plantain afford increased percent sorption of Pb^{2+} over the unmodified version from simulated aqueous solution? What are the optimum conditions for sorption of Pb^{2+} from a simulated aqueous solution using unmodified and citric-acid modified plantain peels?

II. Materials and Methods
2.1 Materials and Instrumentation
Pb(NO$_3$)$_2$, citric acid, HNO$_3$, NaOH used were of analytical grade. Laboratory test sieve (Endecotts Ltd London, England, Serial No: 6085504) was used to sieve biomass used. Atomic Absorption Spectrophotometer (Buck Scientific) was employed for determination residual metal ion concentration. Fourier transform-Infra spectrophotometer (Shimadzu Corporation) was used for functional group identification. Whatman filter paper (No. 1) filter paper was used to separate metal laden biomass from aqueous solution.

2.2 Methods
2.2.1 *Preparation of plantain peels adsorbents – unmodified and citric acid-modified*
Plantain peels were collected from small scale local plantain roasters in Akure, Ondo state, Nigeria. Two roasters were from the Federal University of Technology Akure (FUTA) area, one from Akure main market and the last from Akure-Ilesa road, Akure, Ondo state. The peels were thoroughly washed with deionized water and dried. After complete drying, they were ground and sieved to particle sizes between 300 – 1100 μm which were collected, mixed and used for the study. Peels were treated with HNO$_3$ and NaOH. Following the method of [5] with slight modification, 500 g of ground plantain peels (GPP) were treated with 5 litres 0.1 M HNO$_3$ for 2 h in order to demineralise peels. Peels were then washed with 5 litres of deionized water and dried. Next, 350 g of acid treated-ground plantain peels (AT-GPP) were treated with 7 litres, 0.1 M NaOH by soaking for 2 h, filtered and rinsed thrice with a total of 10 litres of deionized water and dried. Base treated ground plantain peel (BT-GPP) was modified with citric acid. Ground Plantain peel obtained after both acid and base treatments (AT-GPP and BT-GPP) will be referred to as unmodified ground plantain peels (Un-GPP). Ninety grams of Un-GPP was treated with 900 ml, 0.6 M citric acid at 80 C for 1.5 h in order to introduce carboxylate groups on its surface referred to as citric-acid modified ground plantain peels (CA-GPP). CA-GPP was washed thrice with a total of 2 L of deionized water. Finally, it was dried at 60° C. Fourier transform – Infrared Spectroscopy (FT-IR) was employed for the characterization of Un-GPP and CA-GPP.

2.2.2 *Preparation of synthetic Pb^{2+} aqueous solution*
All synthetic Pb^{2+} aqueous solution used for this study were prepared by dilution from a 1000 mg/L stock solution. Typically, the 1000 mg/L stock solution was prepared by dissolving 1.599 g of Pb(NO$_3$)$_2$ in 1 L deionized water.

2.2.3 *Batch adsorption studies*
All batch adsorption studies were undertaken at room temperature except otherwise stated. 0.5 g of adsorbent was contacted with 50 ml, 50 mg/L synthetic Pb^{2+} aqueous solution without shaking. pH studies were undertaken by varying pH of Pb^{2+} solution from 3 to 8. Contact time studies were undertaken by varying time

from 30 to 180 min at pH 7 for Un-GPP and pH 5 for CA-GPP. For Un-GPP, time studies were extended to 10 and 20 mins after obtaining maximum adsorption at 30 mins. Adsorbent dose was varied from 0.3 to 0.7 g at same pH used in contact time study but for 30 min (using Un-GPP) and 120 min (with CA-GPP). Temperature and adsorbate concentration studies were co-undertaken by variation of temperature from 308 to 328 K and adsorbate concentration from 25 to 100 mg/L. In this study, adsorbent dose was 0.4 g for Un-GPP and 0.5 g for CA-GPP. Percentage Pb^{2+} adsorbed was calculated using the equation below:

$$\frac{C_i - C_f}{C_i} \times 100$$

(1)

where C$_i$ = initial Pb^{2+} concentration

C$_f$ = final Pb^{2+} concentration after adsorption

2.2.4   Kinetic, Isotherm and Thermodynamic Studies
Kinetic studies
Pseudo-first-order and pseudo-second-order models were applied and the mathematical relations are given below:
Pseudo-first-order:

$$log(q_e - q_t) = log\, q_e - \left(\frac{k_1}{2.303}\right) t$$

(2)

Pseduo-second order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(3)

where: k$_1$ (min^{-1}) and k$_2$ (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order reactions respectively; q$_e$ denotes the adsorption amount (mg g^{-1}).
The mathematical relation:

$$h = k_2 q_e^2$$

(4)

can be used to calculate the initial sorption rate denoted by *h* (g mg^{-1} min^{-1})

Adsorption isotherms
To determine the nature of adsorption, data for both CA-GPP and Un-GPP were fitted into Langmuir and Freundlich isotherms. Langmuir isotherm defines a monolayer adsorption according to the mathematical relation given below:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m}$$

(5)

where q$_e$ is the amount of Pb^{2+} adsorbed per unit mass at equilibrium (mg/g); q$_m$ is the maximum adsorbate that can be adsorbed per unit mass of adsorbent (mg/g); K$_L$ is the adsorption equilibrium constant and C$_e$ is the concentration of adsorbent (mg/L). To obtain a suitable graph, a plot of 1/q$_e$ against 1/C$_e$ was made to yield values for the constants.
Freundlich isotherm defines a heterogeneous adsorption that involves multiple surfaces of suitable energy [27]. It assumes the uptake of the metal ions changes with the distribution of adsorption sites and surface energies. It is represented by the mathematical relation below:

$$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e$$

(6)

where C$_e$ (mg/L) and q$_e$ (mg/g) are the equilibrium concentration of adsorbent in the solution and the amount of adsorbent adsorbed at equilibrium respectively; *n* represents adsorption intensity and K$_F$ (mg$^{1-1/n}$L$^{1/n}$g^{-1}) denotes the adsorption capacity for the adsorbent. The values of the constants were obtained by plotting log q$_e$ against log C$_e$

Thermodynamic studies
In determining the enthalpy, entropy and the Gibb's free energy, the following mathematical equations were employed:

$$\Delta G = \Delta H - T\Delta S$$

(7)

$$ln\, K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

(8)

$$\Delta G = -RT\, ln K$$

(9)

where *K* is the adsorption equilibrium constant. ΔS, ΔG and ΔH represent the entropy changes (JK^{-1}mol^{-1}), Gibbs energy (KJ mol^{-1}) and enthalpy (KJ mol^{-1}). Temperature is represented with T (Kelvin) and R stands for the molar gas constant (J mol^{-1}K^{-1}). To obtain the values of the thermodynamic parameters for both CA-GPP and Un-GPP, a graph of ln K was plotted against 1/T and from the slope and intercept obtained; the parameters were calculated out using relevant mathematical equations.

2.2.5 *Statistical analysis*
Studies were undertaken in duplicates. Data were analyzed using Microsoft Excel® 2007.

III. Results and Discussion
3.1 **Modification and Characterization of plantain peels**
The citric acid modification was undertaken to provide potentially additional binding sites in the form of carboxylic groups on the surface of Un-GPP. Fig. 1a and Fig. 1b show FT-IR spectra of Un-GPP and CA-GPP. Prominent among the peaks in Fig. 1a are those at 3417, 3350, 3308, 2924, 2359, 1641, 1076 and 1024 cm^{-1}. The peaks from 3417 to 3308 cm^{-1} represent OH stretch (alcohol and carboxylic acid). This assignment is confirmed by the presence of a peak at 2924 cm^{-1} which also represents an OH from carboxylic acid. Tannins (e.g. gallic acid), present in plantain peels may be responsible for the observed carboxylic functional group [32]. Also, cellulose and hemicelluloses which have appreciable amount of OH groups may be responsible for some of the OH signals observed [31]. The peak at 1641 cm^{-1} represents a C=C stretch. Unsaturated carbon-carbon bonds are found in some polyphenols. Last, the peak at 1024 cm^{-1} refers to =C-O-C symmetric and asymmetric stretch. Ether linkages of this type are again found in some polyphenols like tannin [32]. Fig. 1b presents IR spectrum of modified plantain peels. It is observed that two new sharp peaks at 1716 and 1541 cm^{-1} appear. Peak at 1716 cm^{-1} hints at a C=O stretch in carboxylic acids. It can also depict C=O stretch in esters. This assignment can be confirmed by the equally present peak at 1238 cm^{-1} (C=O for esters), 1157 cm^{-1} (for aliphatic carboxylates) and 1317 cm^{-1} (for aromatic carboxylates). It is very likely that free carboxylic groups remain on the surface of modified biomass since not all are esterified by OH groups in the biomass (scheme 1). Consequently, the peak at 1716 cm^{-1} hints at the fact that the plantain was modified with citric acid.
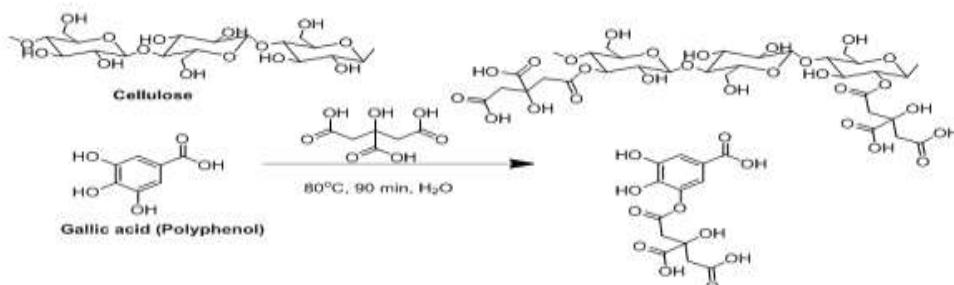
Scheme 1. Suggested scheme for citric acid modification of plantain peels.
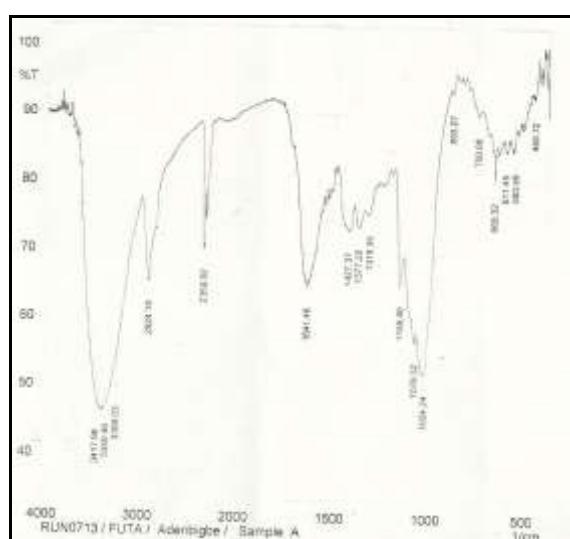
Figure 1a: FT-IR spectrum of unmodified ground plantain peels
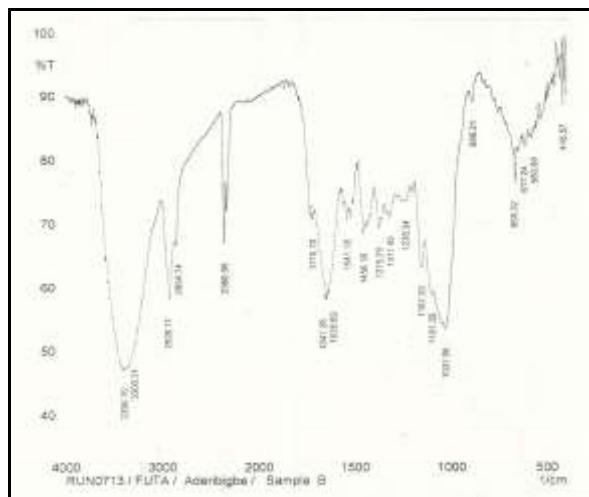
Figure 1b: FT-IR spectrum of citric acid-modified ground plantain peel

3.2 Effect of pH

pH is a very important parameter in adsorption studies as it has been observed from previous studies that different amount of metal ions are adsorbed at varying pH values. The effect of pH was investigated at a range from 3.0 to 8.0 (Fig. 2). Results obtained showed that the pH variation had an effect on the adsorption of Pb^{2+} unto both Un-GPP and CA-GPP. Maximum adsorption was noticed at pH 3 and pH 5 for Un-GPP and CA-GPP respectively. Below pH 3 for Un-GPP, it is likely that there is competition for available carboxylate (COO^{-}) adsorption sites between protons (H^{+}) and Pb^{2+} which perhaps explains why amount of Pb^{2+} taken up by the sorbent was low. It is very likely that precipitation of Pb^{2+} (in the form of Pb(OH)$_2$) began at pH 5, which perhaps explains why less Pb^{2+} was sorbed after pH 5 [19, 26]. This observation was consistent with results obtained in [2], [3], [22] and [25] and in contrast with findings observed in [5] and the most probable reason for this is the presence of –NH$_2$ and –NH linkages in the modifier used.
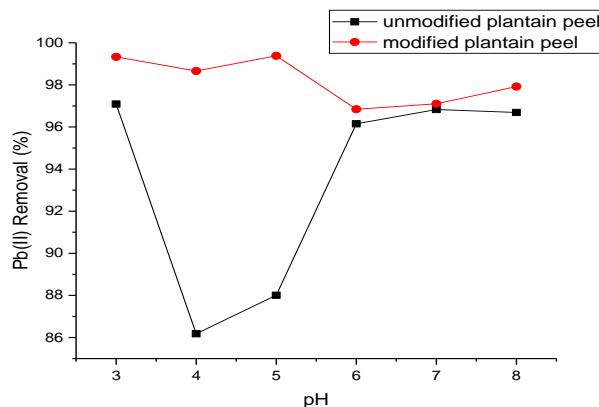
Figure 2: Removal of Pb (II) ions by citric acid- modified and unmodified ground plantain peels at different pH values

3.3 Effect of contact time

To properly investigate the effects of contact time on the adsorption rate of the metal ions by the plantain peels, the experiment was carried out at different contact times (30, 60, 90, 120, 150 and 180 minutes). The results for Un-GPP and CA-GPP are displayed in Fig. 3. Sorption of metal ions is strongly dependent on the concentration of the feed [20] and since the same initial concentration of the feed was used, the availability of adsorption sites on the adsorbent may have led to the different rates observed for Un-GPP and CA-GPP - maximum adsorption was noticed at 30 minutes for Un-GPP but was different for CA-GPP - 120 min. The modifying agent contributed COO^{-} linkages and also increased the H^{+} concentration, likely providing more adsorption sites. There is a possibility that a rapid sorption of the Pb^{2+} had occurred before the 30 min - mark. Results obtained showed that contact times beyond 30 min led to imbalances in the % amount of Pb^{2+} adsorbed as sorption and desorption occurred simultaneously.
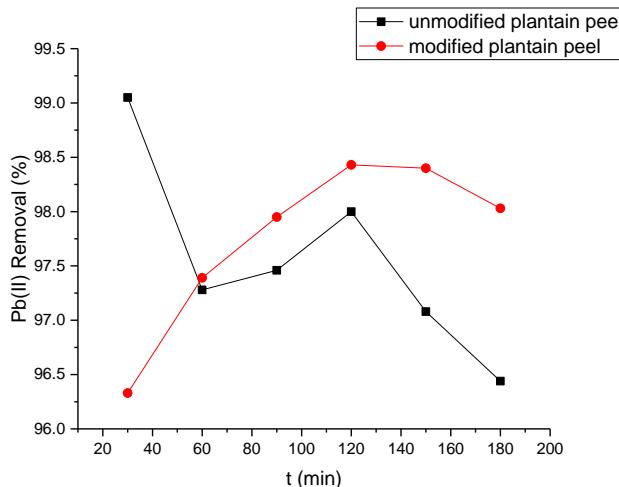
Figure 3: Percentage removal of lead ions at a range of contact times

To ascertain if contact times lower than 30 min will lead to an increase in the % amount of Pb^{2+} adsorbed, experiments were carried out at contact times of 10 min and 20 min and the results showed that the migration of the Pb^{2+} unto the adsorbent was slower than all other contact times under consideration (for Un-GPP). A steady rise was noticed for the % amount of Pb^{2+} adsorbed by the modified plantain peels at contact times between 30 and 120 minutes. Beyond, 120 min, lower amounts of Pb^{2+} were adsorbed. This is probable that rates of desorption exceeded rates of adsorption at contact times greater than 120 min.

3.4 Effect of adsorbent dosage

The dependence of the adsorption of Pb^{2+} on the dosage of the plantain peels used was investigated and adsorbent dose was varied between 0.3 and 0.7 g of plantain peels. For Un-GPP and CA-GPP, an increase in the adsorbent dosage (from 0.3 to 0.4 g) led to a corresponding increase of the % amount of Pb^{2+} adsorbed. This may be due to increase in adsorption sites after dosage increase. Results for Un-GPP showed that at a particular point, increase in the dosage of the adsorbent does not necessarily increase the % amount of Pb^{2+} adsorbed as the already-available adsorption sites is sufficient enough for sorption. Comparison of the % amount of adsorption of Pb^{2+} by Un-GPP with that of CA-GPP showed that the latter had more adsorption sites and bonding linkages leading to an increase in sorption rates. It will be noticed that further increase in adsorbent dosage leads to a decrease in % adsorption. This is as a result of increase in adsorption density which causes an aggregation of adsorption sites hence limiting the capacity for effective adsorption.
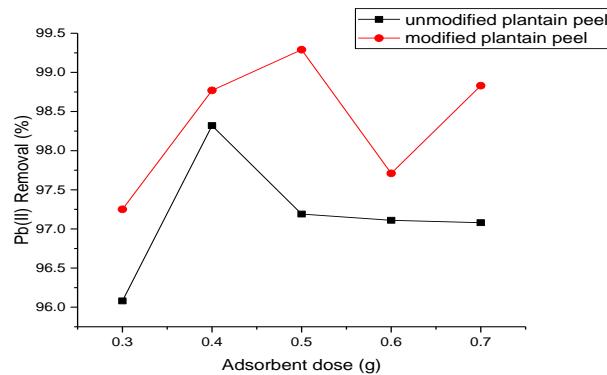
Figure 4: Effect of increase in adsorbent dosage on the percentage removal of lead ions.

3.5 Effect of temperature

Experiments were carried out at temperatures of 308, 318 and 328 K to ascertain the effects of temperature variation on the % adsorption of the Pb^{2+}. Adsorbate concentrations of 25, 50 and 100 mg/L were employed. Results are displayed in Fig. 5. Temperature rise from 308 K to 328 K showed certain adsorption behaviour of Un-GPP. For initial adsorbate concentration of 25 mg/L, the amount of Pb^{2+} ions adsorbed decreased with increase in temperature. Temperature rising is known to result into acceleration of the rate of

diffusion of the lead ions and also complexation of the ions with the functional groups of the adsorbent [5]. The anomaly observed for Un-GPP biomass may be due to its inability to form strong linkages with the metal ions at that concentration. An increase of adsorbent concentration to 50mg/L resulted into increased adsorption with increase in temperature. The interactions between the Pb^{2+} ions and the active groups of the biomass became stronger at higher adsorbate concentration and higher temperature. The increase of temperature to 308 K from 328 K for initial adsorbate concentration of 100mg/L showed a decrease in amount of ions adsorbed; though a peak value was obtained at 318 K (for Un-GPP) while a sharp downward decrease was observed for the modified biomass. It shows that for this concentration, increase in temperature at a point causes migration of the ions back to the aqueous solution.

Citric acid which is used as the modifier has a considerable high solubility in water when there is a steady increase in temperature. It can be inferred that the metal ions which have been adsorbed on the citric acid-linkages in the adsorbent tend to migrate back to the water. For the concentration effect, a different trend was observed for Un-GPP. For all temperatures (308, 318 and 328 K), an increased initial adsorbate concentration of 100 mg/L resulted into the highest amount of adsorption (97.35%, 97.73% and 96.49% respectively). It can be inferred that for adsorption behaviour of Un-GPP, there is an increased adsorption of Pb^{2+} when temperature is kept constant and initial adsorbate concentration is increased.
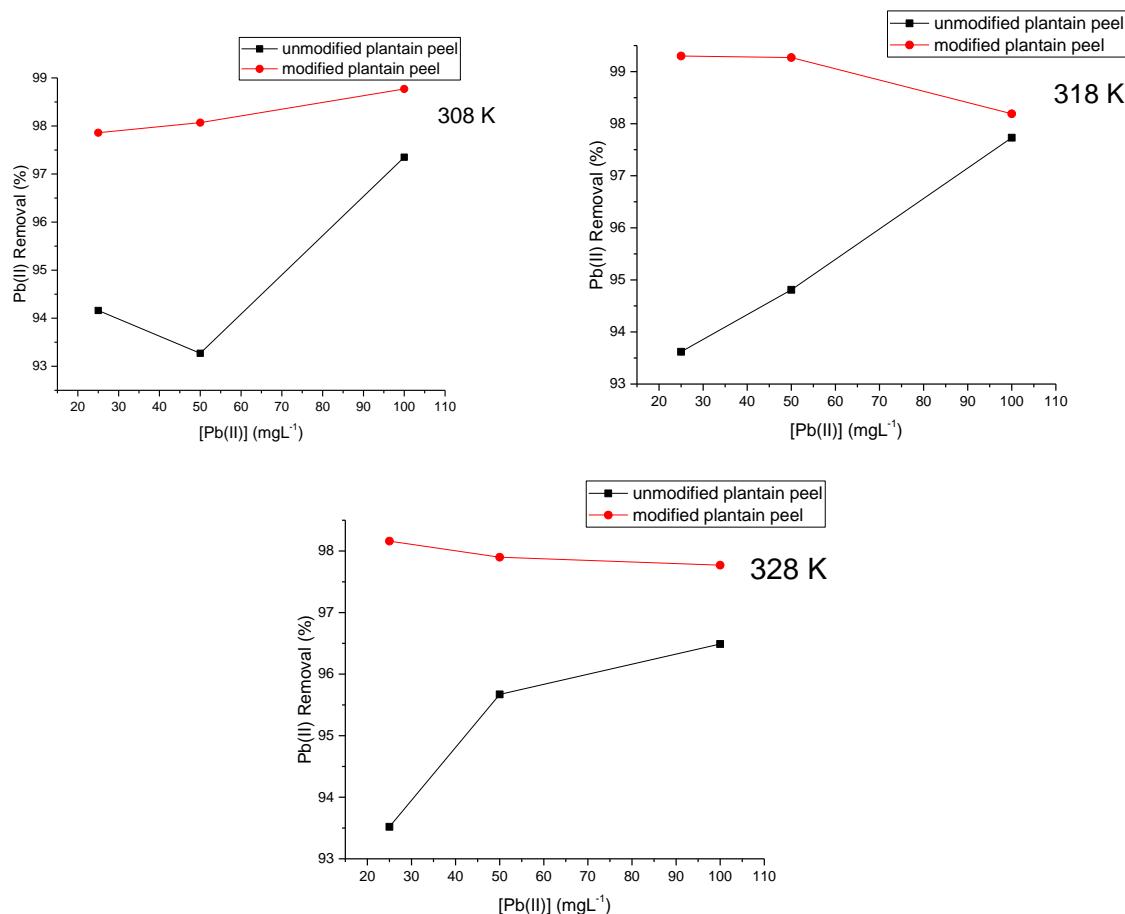
Figure 5: Behaviour of the percentage adsorption of lead ions by the bio-sorbents at different temperatures

For the modified biomass, temperature rise from 308 K to 328 K at adsorbate concentration of 25 mg/L resulted to a corresponding increase of Pb^{2+} adsorbed. The deficiency that was encountered by Un-GPP at this concentration must have been overcome by the extra linkages provided by the modifying agent. Temperature increase led to a decrease in adsorption rate at initial adsorbate concentration of 50 mg/L and 100 mg/L. The maximum % adsorption of the Pb^{2+} for Un-GPP and CA-GPP were 95.73% (at adsorbate concentration of 100 mg/L and temperature of 318 K) and 99.3% (at adsorbate concentration of 25 mg/L and temperature of 318 K) respectively. The summary of this is that Un-GPP requires high adsorbate concentration to compensate for the absence of a modifying agent unlike CA-GPP which requires a relatively-lower concentration. A moderate temperature is convenient for both as the maximum adsorptions took place at 318 K.

3.6 Kinetic Studies

Kinetic models were applied to the experimental data to study the mechanism of adsorption. The values of the constants were obtained by making necessary plots as guided by the kinetic models and the results are shown in

Table 1: Values of constants obtained when experimental data was fitted to both pseudo-first-order and second-order kinetic models.

	Pseudo-first-order		
	K$_1$ (min^{-1})	q$_e$ (mg g^{-1})	R^2
CA-GPP	0.0046	1.74	0.6457
Un-GPP	0.0062	1.70	0.5694

	Pseudo-second order			
	K$_2$ (g mg^{-1} min^{-1})	q$_e$ (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2
CA-GPP	0.0338	49.26	82.02	1.0000
Un-GPP	0.1764	47.62	400.02	0.9926

The correlation coefficient values for the pseudo-second-order model were higher than that of the pseudo-first-order reaction and this suggests that the pseudo-second-order kinetic model fits the experimental data better. The insufficiency of the first order model to fit the kinetics may be due to the limitations of the boundary layer controlling the adsorption [1]. For the pseudo-second-order kinetics, the experimental adsorption capacity values with those of the calculated were very close.

Table 2: Maximum lead adsorption capacities and pH of previous studies.

Adsorbent	q$_e$ (mg/g)	pH	References
Groundnut husk modified with Guar Gum	9.76	5.0	Rais A. *et al* [3]
Ion-imprinted tetraethylene pentamine modified chitosan beads	259.68	6.0	Bingjie L.*et al* [5]
Activated carbon	26.60	4.5	Sekar *et al* [28]
Oak biochar	13.10	5.0	Mohan *et al* [29]
Pinewood biochar	3.00	5.0	Mohan *et al* [29]
Carbon nanotubes	92.30	5.7	Tian *et al* [30]
Ethylene diamine-modified yeast biomass coated with magnetic chitosan microparticles	134.90	6.0	Ting-ting L. *et al* [21]
Surfactant-modified diatomaceous earth	23.58	5.0	Rund A.A. *et al* [22]
Unmodified ground plantain peels	47.62	3.0	**This work**
Citric acid-modified ground plantain peels	49.26	5.0	**This work**

Results displayed in TABLE 2 showed that the adsorption capacities of Un-GPP and CA-GPP when compared with previous studies were relatively good; with the modified form showing greater capacity. The pH at which maximum adsorption took place for the modified biomass was consistent with results obtained in [22], [31], [30], [29] and [3]. This is due to the fact that the formation of lead hydroxides at pH greater than 5 is very feasible [26]. However, previous studies showed that few maximum adsorptions took place at higher and lower pH values (for instance, the unmodified biomass).

The correlation values for CA-GPP were higher than those of Un-GPP in both the pseudo-first-order and pseudo-second-order models and the q$_e$ values of CA-GPP followed the same pattern and this shows that CA-GPP has the capacity to adsorb more quantity of Pb^{2+} than Un-GPP.

3.7 Adsorption Isotherms

It is very useful to understand the mechanism that governed the adsorption process of Pb^{2+} unto Un-GPP and CA-GPP. To this end, Langmuir and Freundlich isotherms were employed. One importance of establishing the predominant adsorption mechanism is to ascertain if chemical modification was necessary in the first place. Results obtained are displayed in TABLE 3.

Table 3: Values of constants obtained when experimental data for Un-GPP and CA-GPP were fitted to Langmuir and Freundlich isotherm models.

Langmuir isotherm	q$_m$	K$_L$	R^2
CA-GPP	0.0625	11.147	0.0435
Un-GPP	8.826	1.1350	0.1714
Freundlich isotherm	**n**	**K$_F$**	**R^2**
CA-GPP	4.62	0.0055	0.1287
Un-GPP	11.64	0.0049	0.0063

Based on the R^2 values, the experimental data for Un-GPP were better described by Langmuir isotherm. It indicated that Un-GPP involves a dominant monolayer adsorption. For CA-GPP, the data were better fitted by the Freundlich isotherm; signifying a heterogenous adsorption. This was consistent with results obtained in [3], [33], [34] and [35]. This can be traced to the effect of the modifying agent (citric acid) which brought in additional surface sites. The greater value of K_L for CA-GPP than Un-GPP signifies that the adsorption of the Pb^{2+} was stronger for the modified biomass.

When the values of *n* in Freundlich isotherm are between 2 and 10, it signifies strong adsorption of the ions unto the adsorbent. This is consistent with what was obtained for Langmuir isotherm as the *n* values were on the high side.

3.8 Thermodynamic studies

It is very pertinent to carry out thermodynamic studies to investigate the spontaneity of the process. The results of the thermodynamic parameters for both Un-GPP and CA-GPP were displayed in TABLE 4.

Table 4: Values of thermodynamic parameters obtained for the adsorption reactions by unmodified and citric acid-modified ground plantain peels.

	Temperature (K)	ΔH (KJ/mol)	ΔS (J/K/mol)	ΔG (KJ/mol)
	308			22.98
Un-GPP	318	19.61	-10.92	23.09
	328			23.2
	308			-12.68
CA-GPP	318	2.696	49.92	-13.18

Negative values were obtained for the Gibb's free energy (-12.68, -13.18 and -13.68 KJ/mol) and these indicate that the adsorption process of the Pb^{2+} by the modified biomass was spontaneous in nature and there was a marked increase in spontaneity with increasing temperature. With increase in temperature, there is a decrease of the boundary layer surrounding the adsorbent, facilitating easy attachment of adsorbate molecules onto adsorbent surface and hence the increase in spontaneity. The results on the other hand, showed non-spontaneity for Un-GPP; increase in temperature led to a decrease in spontaneity.

There is reduced disorderliness in Un-GPP as non-spontaneity increase with temperature. The growth of randomness as a result of structural changes in both the adsorbent and adsorbate during adsorption was responsible for the high disorderliness in the modified biomass. Both Un-GPP and CA-GPP had positive enthalpy values showing that the reaction was endothermic with the modified biomass releasing lesser energy. The positive values obtained for the enthalpy also suggests that the adsorption process was more of chemisorption than physisorption [1].

IV. Conclusion

This study shows that plantain peels can be chemically modified by citric acid. Also, it was observed that citric-acid modified ground plantain peels can remove more Pb^{2+} than the unmodified version from simulated aqueous solution containing only the metal ion. The adsorption processes using unmodified and citric acid-modified ground plantain peels were pH, contact time, adsorbent dose, adsorbate concentration and temperature dependent. Sorption of Pb^{2+} by both adsorbents was observed to be majorly a pseudo-second order process. Physisorption was the predominant mechanism when citric-acid modified peels were contacted with Pb^{2+} while it was chemisorption when unmodified peels were used for the same metal. Therefore, chemical modification of ground plantain peels using citric acid helped improve the sorption capacity of the adsorbent for Pb^{2+} removal from a simulated aqueous solution containing only the metal.

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