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# Eco-Friendly Lead Removal: Utilizing Modified and Unmodified Avocado Seed as a Low-Cost Biosorbent.

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**ABSTRACT**
The removal of toxic heavy metal ions, particularly lead, from water sources remains a critical environmental and public health challenge. Existing remediation technologies are often costly and inaccessible, necessitating the exploration of sustainable, low-cost alternatives. This study investigated the potential of alkaline, acid-modified, and unmodified avocado seed (*Persea americana)*, an agricultural waste, as a natural adsorbent for lead removal from aqueous solutions. Using a batch adsorption method, key parameters including; pH, contact time, temperature, adsorbent dosage, and adsorbate concentration were systematically analyzed. Optimal adsorption efficiencies were achieved with both acid and alkaline-modified adsorbent than unmodified adsorbent at pH 5 with an initial lead concentration of 10 ppm, 0.1g of adsorbent, temperature of 60 ºC, and a contact time of 90 minutes. The adsorption process for the acid-modified adsorbent followed the Langmuir isotherm model and exhibited pseudo-second-order kinetics, indicating monolayer adsorption and chemisorption as the dominant mechanism. For the alkaline-modified adsorbent, a correlation coefficient ($R^2$) of 0.9165 shows perfect conformity with the Freundlich model and exhibits pseudo-second-order kinetics. The percentage removal of lead at varying concentrations of the adsorbate was 99.96% for the acid-modified, 99.05 % for the alkaline-modified modified, and 89.99 % for the unmodified adsorbent. These findings highlight modification as a more effective method of increasing the binding sites on adsorbent surfaces and adsorption as being highly pH dependent.

**Keywords:**
Adsorption
Heavy metals
Acid
Alkaline
Isotherm

## 1. INTRODUCTION

The severity of heavy metal contamination especially with lead (Pb) has become a global concern due to its threat to both environmental and public health (Heraldy *et al.,* 2018). Lead pollution is majorly linked to anthropogenic activities such as mining activities, indiscriminate waste disposal, and untreated industrial waste discharges among many others. Lead exposure even at low concentrations has been identified to cause developmental disorders in children, neurological damage, and kidney failure according to the Agency for Toxic Substances and Disease Registry (ATSDR,2020). Elimination of lead in the environment becomes imperative due to the **non-**

**biodegradability** and bioaccumulation nature of the metal.

Several successful records on conventional lead remediation techniques have been reported such as ion exchange (Goyal *et al.,* 2020; Jasim and Ajjam, 2024), membrane filtration (Zhang *et al.,* 2021; Amiri, *et al.,* 2021), electrochemical treatment (Chegeni *et al.,* 2021; Choumane and Peulon 2021), oxidation process (Salih and Ibrahim 2024; Li*, et al.,* 2020) and chemical precipitation (Zhang, *et al.,* 2020). DuEnergyntensity, non-cost effectiveness, and se, secondary waste generation necessitated the exploration of a sustainable alternative. In this plight, adsorption with the use of biosorbent has attracted significant attention as an eco-friendly approach to a wide range of heavy metal removal (Ergüvenerler *et al.,* 2020). The technique has been employed in the removal of chromium (Shakya and Agarwa 2019), Mercury (Song *et al.,* 2014), Zinc (Sangeetha *et al.,* 2019), Nickel (Shen *et al.,* 2017), and several others.

Application of adsorption to agricultural wastes is capable of metal binding which presents an attractive solution for water treatment. Reports on the treatment of heavy metal contamination with a wide range of agricultural wastes are well documented; cadmium treatment with orange peel (Abou-Elkassem *et al.,* 2022), cadmium and lead with corn straw (Chi *et al.,* 2017). Others include nickel removal with rice husk (Shen *et al.,* 2017), adsorption of chromium with pineapple peels (Shakya and Agarwal, 2019), and coconut shell for arsenic ion removal (Dakheel *et al.,* 2022), etc. Agricultural wastes are rich in lignin, cellulose, and functional groups capable of adsorbing metal ions.

Avocado seeds (*Persea americana*), an agricultural by-product, offer promising potential as an alternative biosorbent due to their porous structure and the presence of active binding sites (Ayangbenro and Babalola 2020). However, natural adsorbents often require surface modification to enhance their adsorption efficiency (Song *et al.,* 2014). Chemical treatments, such as acid and alkaline modifications, can significantly improve the binding capacity of these materials by increasing the availability of functional groups involved in metal ion chelation.

This study evaluates the efficacy of unmodified, acid-modified, and alkaline-modified avocado seeds in removing lead from aqueous solutions. By systematically analyzing the effects of pH, contact time, temperature, adsorbent dosage, and adsorbate concentration, this research aims to identify optimal adsorption conditions and elucidate the underlying mechanisms governing the process. The findings from this study are expected to contribute to the growing body of knowledge on low-cost biosorption techniques and underscore the potential of modified avocado seed as a sustainable solution for the treatment of lead-contaminated water.

## 2. MATERIALS AND METHOD

### *2.1. Analytical and statistical procedure*

The avocado seeds *(Persea americana)* were collected, washed, cut into smaller pieces, air dr i e d, and placed in an oven at a temperature of 80°C until they became very dried and crispy. The dried seeds were ground into fine powder using a mechanical grinder. Half of the sample was modified chemically with 0.1M of NaOH. The other half was acid-modified by soaking in 0.1 M $H_2SO4$ for 24 hours, followed by repeated washing with distilled water to eliminate soluble impurities. The pH level was monitored using an electronic pH meter until a neutral pH of 7 was achieved. To eliminate any remaining physical impurities, both alkaline and acid-modified powder were oven-dried again at 80°C.

### *Preparation of Stock Solution*

A stock solution with a concentration of 1000 ppm of the lead metal ion was prepared by dissolving 0.39 g of the metal salt (lead nitrate) into a 250 ml volumetric flask and filling the flask to its maximum volume with distilled water. Various adsorbate concentrations (10, 20, 30, 40, and 50 ppm) were prepared from stock solution by serial dilution with distilled water.

***Batch Biosorption***

Batch adsorption studies were conducted using 100 ml beakers into which the lead solution was poured in and the weighed ground avocado seed powder was added. The beakers each containing the solution of lead ion and ground avocado seed were agitated on an electric orbital shaker at a constant speed of 200 rpm at a shaking time of 60 mins, the samples were then withdrawn and filtered using Whatman No. 1 filter paper. This procedure was repeated using the acid and alkaline modified. The filtrates were analyzed for residual lead concentrations using an Atomic Absorption Spectrophotometer (AAS).

The effect of adsorbent dose was determined by weighing various dosages of 0.2, 0.4, 0.6, 0.8, to 1.0 g into different beakers containing 20 ml of 10 ppm lead solution. The pH was kept neutral at 7. The beakers were agitated at a constant speed of 200 rpm for 60 mins. The same procedure was observed for the effect of initial concentration, contact time, temperature, and pH. Thereafter, the mixtures were filtered and the concentration of lead in the filtrate was analyzed using AAS. The percentage of lead removed by the avocado seed was calculated from the difference between the initial lead concentration ($C_o$) and the final lead concentration ($C_f$) using the formula shown in the equation below.

***2.2. Equations***

$$\% \, Removal = \frac{C_o - C_f}{C_o} \, x \, 100 \qquad (1)$$

The amount of lead ions adsorbed ($q_e$) by the biomaterial was calculated with the formula;

$$q_e = \frac{V(C_o - C_f)}{m} \, x \, 100 \qquad (2)$$

where; m = mass of the adsorbent and V = volume of adsorbate

**Adsorption Isotherm**

Langmuir and Freundlich adsorption isotherms were used to analyze experimental equilibrium sorption. Langmuir equation according to Ozacar *et al.,* 2005 was employed. The equation is represented thus:

$$\frac{C_e}{q_e} = K_L \frac{1}{Q_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

where $K_L$ (l/g) = Langmuir adsorption constant/desorption energy; $q_{max}$ = maximum sorption upon complete saturation of the biomass surface.

This describes the adsorption capacity of the avocado seed over the uptake of lead ions. $K_L$ is related to the sorption energy. It is the affinity of the adsorbent toward the adsorbate. The high value of $K_L$ implies a strong binding force. The values of $q_{max}$ and $K_L$ are calculated from the slope and intercept of the linear plot of $C_e/q_e$ versus $C_e$. Other parameters are as described earlier. The experimental data were fitted into the Langmuir equation by plotting $C_e/q_e$ against $C_e$. The equation for Freundlich isotherm is given as

$$Log q_e = log K_F + \frac{1}{n} log C_e \qquad (4)$$

where where $K_f$ and n are Freundlich constants. The value of n indicates the affinity of the adsorbate towards the biomass. The isotherm is obtained by plotting log $q_e$ against log $C_e$.

***Sorption Kinetics***

The integrated forms of sorption kinetic equations employed are Pseudo-first-order kinetics (Ho and Mckay, 1998) and Pseudo-second order kinetics (Ho, 2004) as shown in equations 5 and 6 below

$$Log(q_e - q_t) = Logq_e - K_1 \frac{t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{ho} + \frac{t}{q_e} \quad (6)$$

where $q_e$ and $q_t$ (mg/g) = amount of lead ion adsorbed at equilibrium and given time, t (min) respectively. $K_1$ = rate constant for Pseudo first order equation. $h_o$ = initial sorption rate for Pseudo second order
the equation is given as:

$$\text{ho} = K_2 q_e^2 \quad (7)$$

where $K_2$ = rate constant for Pseudo second order equation. The values obtained from the plots are shown in Tables 4 and 5 below.

## 3. RESULTS AND DISCUSSION

### *3.1. Finding of research*

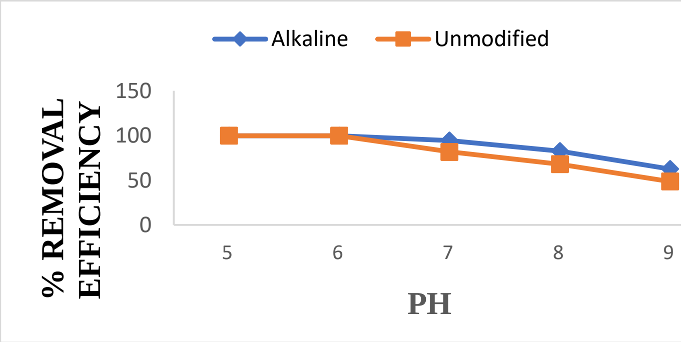


***Figure 1****: Plot of % Removal of lead using alkaline modified adsorbent at varying pH.*

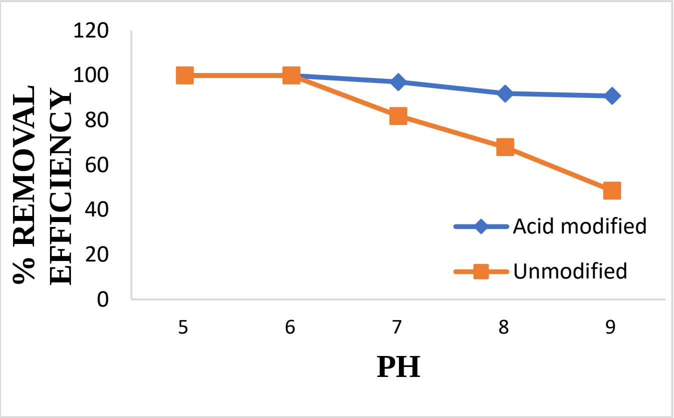


***Figure 2:*** *Plot of % Removal of lead using acid-modified adsorbent at varying pH.*

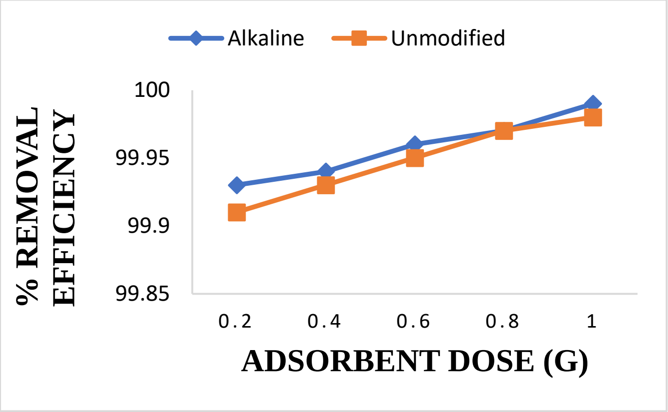


***Figure 3:*** *Plot of % Removal of lead using alkaline modified adsorbent at varying adsorbent doses.*

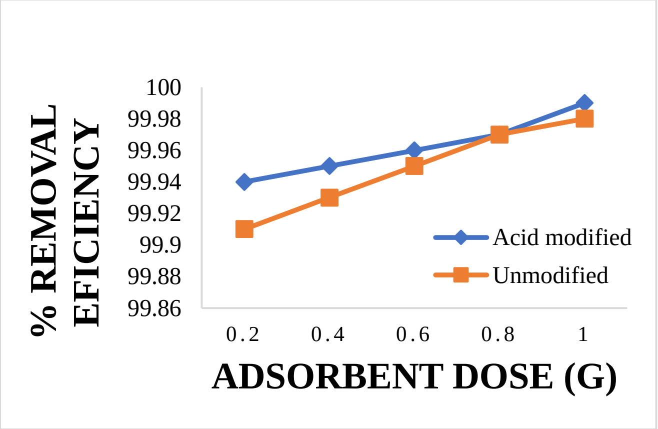


***Figure 4****: Plot of % Removal of lead using acid-modified adsorbent at varying adsorbent doses.*

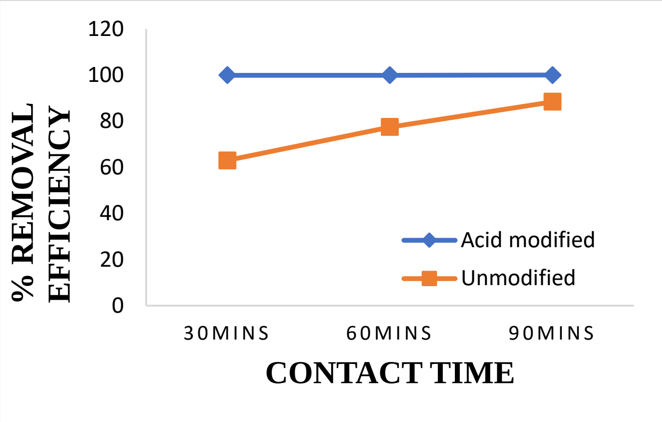


***Figure 5**: Plot of % Removal of lead using acid-modified adsorbent at varying contact time.*

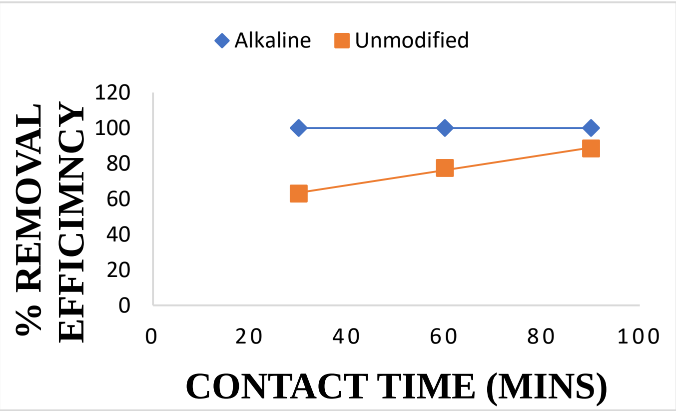


***Figure 6**: Plot of % Removal of lead using alkaline modified adsorbent at varying contact time.*

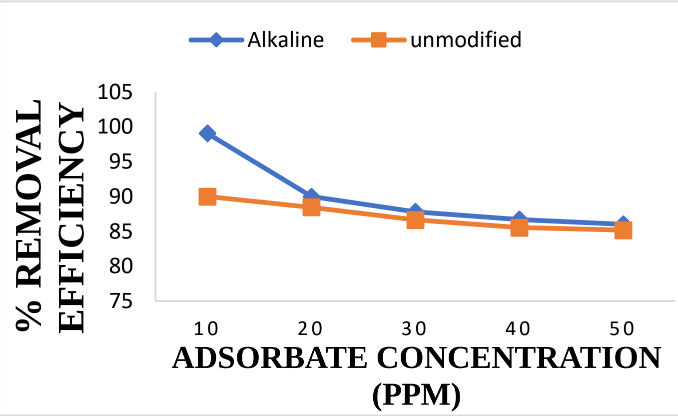


***Figure 7:** Plot of % Removal of lead using alkaline modified adsorbent at varying adsorbate concentrations.*

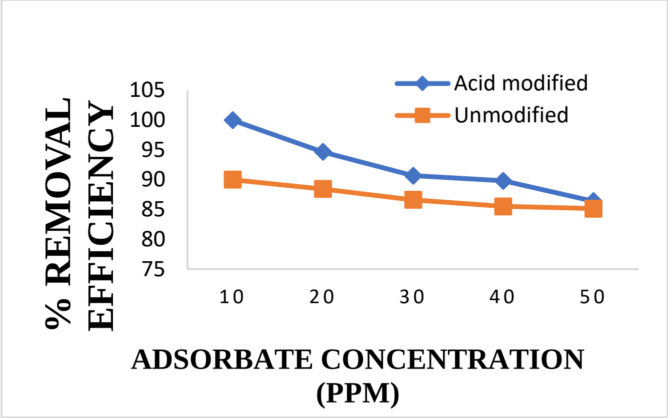


***Figure 8**: Plot of % Removal of lead using acid-modified adsorbent at varying adsorbate concentrations.*

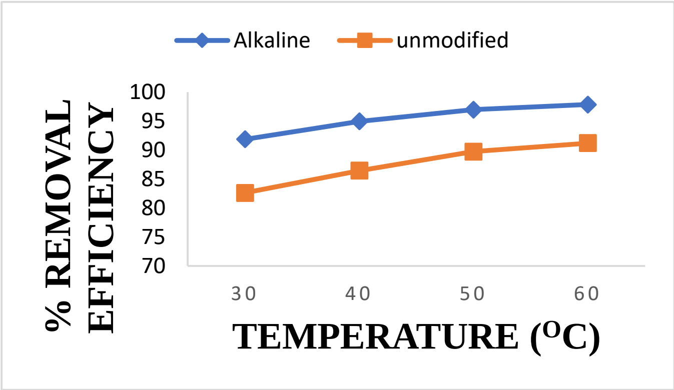


***Figure 9**: Plot of % Removal of lead using alkaline modified adsorbent at varying adsorbate temperatures.*

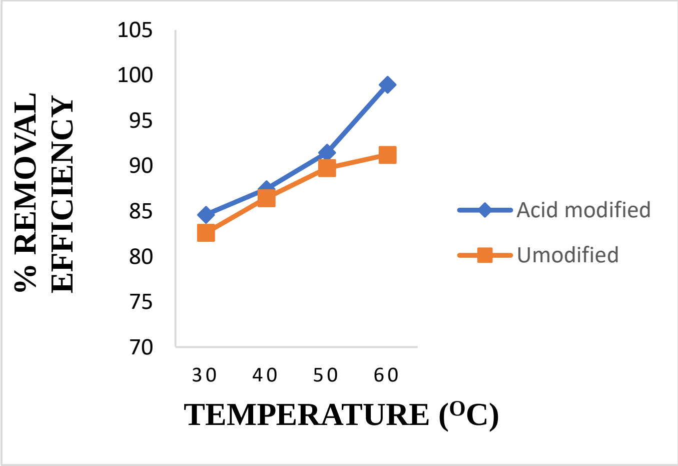


***Figure 10**: Plot of % Removal of lead using acid-*

*modified adsorbent at varying adsorbate temperatures.*

### *3.2. Tables*

**Adsorption Isotherm**

***Table 1:*** *Langmuir and Freundlich Isotherms parameters of Lead ion adsorption onto the acid-modified and unmodified adsorbent.*

| | Langmuir | | |
|---|---|---|---|
| Adsorbent | $q_{max}$(mg/g) | $K_L$(l/mg) | $R^2$ |
| Modified | 5000 | 1.000 | 0.9191 |
| Unmodified | 0.0019 | 1.0712 | 0.9191 |

| | Freundlich | | |
|---|---|---|---|
| Adsorbent | $K_F$(mg/g) | n | $R^2$ |
| Modified | 2449.19 | 5.5617 | 0.8863 |
| Unmodified | 968.213 | 1.3066 | 0.9991 |

***Table 2:*** *Langmuir and Freundlich Isotherms parameters of Lead ion adsorption onto alkaline modified and unmodified adsorbent.*

| | Langmuir | | |
|---|---|---|---|
| Adsorbent | $q_{max}$(mg/g) | $K_L$(l/mg) | $R^2$ |
| Modified | 5000 | 0.05 | 0.8588 |
| Unmodified | 0.0019 | 1.0712 | 0.9963 |

| | Freundlich | | |
|---|---|---|---|
| Adsorbent | $K_F$(mg/g) | n | $R^2$ |
| Modified | 1808.83 | 3447 | 0.9165 |
| Unmodified | 968.213 | 1.3066 | 0.9991 |

***Table 3:*** *Separation Factors (RL) Values for alkaline, acid, and unmodified avocado seeds*

| Concentrations (ppm) | Alkaline seed | Acid seed | Unmodified seed |
|---|---|---|---|
| 10 | 0.667 | 0.090 | 0.085 |
| 20 | 0.500 | 0.047 | 0.030 |
| 30 | 0.400 | 0.032 | 0.022 |
| 40 | 0.333 | 0.024 | 0.022 |
| 50 | 0.285 | 0.019 | 0.018 |

**Sorption Kinetics**

***Table 4:*** *Kinetic Parameters of lead ion adsorption onto acid-modified and unmodified adsorbent*

| | Pseudo-first order | | |
|---|---|---|---|
| Adsorbent | $q_e$ (mg/g) | $K_1$(min$^{-1}$) | $R^2$ |
| Modified | 0.498 | $8.20 \times 10^{-3}$ | 0.9505 |
| Unmodified | 6.430 | $8.3 \times 10^{-3}$ | 0.9334 |

| | Pseudo-second order | | |
|---|---|---|---|
| Adsorbent | $q_e$ (mg/g) | $K_2$ (g/mg/min) | $R^2$ |
| Modified | 1000 | 0.001 | 1 |
| Unmodified | 47.39 | 0.047 | 0.9987 |

***Table 5:*** *Kinetic Parameters of lead ion adsorption onto alkaline modified and unmodified adsorbent*

| | Pseudo-first order | | |
|---|---|---|---|
| Adsorbent | $q_e$ (mg/g) | $K_1$(min$^{-1}$) | $R^2$ |
| Modified | 114.58 | $8.0 \times 10^{-3}$ | 0.9777 |
| Unmodified | 6.430 | $8.3 \times 10^{-3}$ | 0.9334 |

| | Pseudo-second order | | |
|---|---|---|---|
| Adsorbent | $q_e$ (mg/g) | $K_2$ (g/mg/min) | $R^2$ |
| Modified | 1000 | 0.001 | 1 |
| Unmodified | 47.39 | 0.047 | 0.9987 |

## DISCUSSION

### *3.1 Effects of operating conditions*

#### *3.1.1 Effects of pH*

Figures 1 and 2 showed the influence of pH on the adsorption of lead ions by both acid-modified and alkaline-modified avocado seeds respectively. From the plots, the highest percentage removal of lead ions occurred at pH 5, an acidic medium. As the pH increased, a gradual decrease in removal efficiency was observed. This steady decrease can be attributed to an increase in hydroxide ion concentration, which competes with the adsorption sites on the surface of the adsorbent thus resulting in the decrease in the lead removal. A similar observation was made by Nthiga *et al.,* (2016), which was attributed to the introduction of more -OH groups that reacted with the lead ions to form lead hydroxide. The removal efficiency of lead ions by acid-modified and alkaline-modified avocado seed was compared. The results show that the highest amount of lead ion uptake occurred at pH 5 with 99.97% removal.

### 3.1.2 Effects of adsorbent dosage

The impact of varying adsorbent doses is shown in Figures 3 and 4. The results show that increasing the adsorbent dose leads to a corresponding increase in percentage removal. This can be attributed to the greater availability of adsorption sites on adsorbent surface thus reducing competition between the adsorbing lead ion. Bhatnagar and Minocha (2006) have reported similar observations. The removal efficiency of lead ions by acid-modified and alkaline-modified avocado seeds was also compared. Both biomasses show significantly high affinity towards lead ion removal with a 99.99% value at 1.0 g adsorbent dosage.

### 3.1.3 Effects of Contact Time

Figures 5 and 6 revealed the impact of varying contact times on lead ion removal. The results show that as the contact time increased from 30 to 90 mins the percentage removal increased. This may be due to the extended duration, allowing for a more thorough interaction between the adsorbent surface and adsorbate, enhancing adsorption efficiency. Asrari *et al.,* (2010) have reported a similar trend. The removal efficiency of lead ions by the acid-modified and alkaline-modified seed was also compared and the acid-modified avocado seed showed slightly higher affinity towards the lead ion removal than the alkaline modified with values of 99.98% and 99.97% respectively at a contact time of 90 minutes. A similar report on citric acid modification of biomass for successful treatment of heavy metals from the water was stated by Monroy-Figueroa *et al.,* (2015).

### 3.1.4 Effects of adsorbate concentration

The influence of adsorbate concentration on adsorption was investigated at different initial lead ion concentrations varying from 10 – 50 ppm. From Figures 7 and 8, as the adsorbate concentration increased, the percentage removal decreased. At higher concentrations of the adsorbate, the number of available sites on the adsorbent is expected to decrease as more sites are saturated. This results in a decrease in removal efficiency. At lower concentrations more adsorption sites are available thus the efficiency of removal was higher as observed from the plots. In 2016, Nthiga et al reported a decrease in percentage removal with increasing adsorbate concentration. The observed behavior was attributed to the increase in the amount of metal ions as compared to the unchanging number of binding sites on the surface of the powdered avocado seed. The removal efficiency of lead ions by acid-modified and alkaline-modified biomasses was also compared and the acid-modified avocado seed showed higher affinity towards the lead ion removal than the alkaline-modified seed with values of 99.96 and 99.05% respectively at an initial concentration of 10 ppm.

### 3.1.5 Effects of temperature

The effect of temperature on adsorption was investigated at varying temperatures of 30, 40, 50, and 60 $^{o}$C. From Figures 9 and 10, the percentage removal increases with increasing temperature. At higher temperatures, the adsorbate molecules would have possibly acquired greater energy to collide with the adsorbent surface, which enhanced adsorption. A similar report was also given by Ramiro *et al.,* (2013). The adsorption capacity of the modified and unmodified avocado seeds was determined at 60 ºC. It was observed that the modified avocado seed has a higher adsorption capacity of 98.95% with acid-modified and 97.88% with alkaline seed modified.

***3.2 Adsorption Isotherm***

Langmuir and Freundlich adsorption constants were derived from intercepts while n was from the slope of the plots respectively. The values of maximum monolayer coverage ($q_{max}$), obtained from Langmuir plots were positive for both acid and alkaline-modified as well as unmodified adsorbents. High and same correlation coefficient ($R^2$) value of 0.9191 were obtained from Langmuir plots for acid-modified and unmodified biomasses. The values from Freundlich isotherm for unmodified adsorbents are higher than those from acid-modified are. Correlation coefficients for the acid-modified and unmodified adsorbent. The correlation coefficients for alkaline modified and unmodified are best fitted with the Freundlich model with higher values than those of Langmuir for both modified and unmodified biosorbents respectively. The dimensionless separation factor $R_L$, is expressed as:

$$R_L = \frac{1}{1+K_L C_o} \qquad (8)$$

where; $K_L$ is the Langmuir constant and $C_o$ is the initial metal ion concentration.

For this study, $R_L$ values for lead ions adsorption onto acid/alkaline modified and unmodified avocado seeds ranged within the favorable zone (0< RL >1) validating the Langmuir high-suction model. From the data analysis, the Langmuir isotherm fit indicates monolayer adsorption, suggesting a single layer of adsorbate molecules on the adsorbent surface. This adsorption process is chemical in nature (Chemisorption) as evidenced by the increase in percentage removal with an increase in temperature.

**Freundlich**

The Freundlich isotherm analysis revealed adsorption intensity (n) of 5.5617 and 1.306 for acid-modified and unmodified avocado seed respectively, and 3447 and 1.3066 for alkaline-modified and unmodified seed. Despite a moderate correlation coefficient $R^2$ value of 0.8863 and 0.9991 for acid-modified and unmodified avocado seeds as well as 0.9165 and 0.9991for alkaline modified and unmodified adsorbent as seen in Tables I and 2 the usually high n value suggests a significant deviation from the linearity, implying that Freundlich model may not accurately describe the adsorption process (Tran *et al.,* 2017).

***3.3 Sorption Kinetics***

The kinetic data show conformity with the pseudo-second-order kinetics for both the acid-modified and alkaline-modified avocado seed since the correlation coefficient ($R^2$) values are higher than those of the pseudo-first-order in each case. This suggests that the adsorption process followed chemisorption, characterized by strong chemical bonds between the adsorbate and adsorbent surface.

## 4. CONCLUSION

Adsorption of lead with modified avocado seed improves adsorption efficiency. This improvement is attributed to increased surface area, improved functional group availability, and enhanced electrostatic force of attraction between the modified adsorbent and lead ions. Acidified avocado seed has a higher adsorption efficiency for lead ions compared to the alkaline-modified. The interaction between the adsorbate and adsorbent was pH-dependent. Adsorption is affected by contact time, temperature, adsorbent and adsorbate dosages. The isotherm data obtained fitted the Freundlich isotherm well for alkaline-modified avocado seed and the Langmuir model for acid-modified seed indicating monolayer coverage. Kinetic data fitted the Pseudo-second order model, suggesting chemisorption. Future studies should investigate the adsorption of other heavy metals by modified avocado seeds. Conversion of the modified adsorbents into activated carbon for possible industrial applications should be carried out.

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