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Kinetics of Adsorption of Lead, Arsenic, and Cadmium from Solution by Jackfruit Seed (*Artocarpus heterophyllus*): A Batch Adsorption Study

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Abstract: Heavy metals have been implicated in a lot of diseases affecting man today. These heavy metals include Arsenic, Mercury, Zinc, Lead, and Cadmium among others. The study of heavy metals is important as they tend to bio-accumulate, but do not biodegrade in the human body. This has necessitated the need for innovative and cost-effective methods to remove heavy metals from the body and the environment. This study was designed to evaluate the potential of Jackfruit seed (*Artocarpus heterophyllus*) as an adsorbent for heavy metals under varying conditions such as time, particle size, and dose. The powdered jackfruit seed was subjected to sieve analysis, in which sizes 2000µm, 850µm, and 425µm were used for adsorption studies. The samples were analyzed using an Atomic adsorption spectrophotometer (AAS) to check the concentration of metal ions in the solution. The results showed that adsorption of lead>arsenic>cadmium, and varied at different adsorbent doses, contact time, and particle sizes. The equilibrium data of the study was well-fitted for the Langmuir and Freundlich isotherm. They also show that Jackfruit seed has great potential to serve as a cost-effective, environmentally friendly bio-sorbent for heavy metal removal from solution.

Keywords: Heavy Metals, Arsenic, Lead, Cadmium, Bio-sorption, Particle Size, Contact Time, Dose

1. Introduction

Heavy metals are a group of metals that are gradually growing to be a cause for concern, and this is not just because they are toxic even at very low concentrations, it is due to their tendency to bio-accumulate but not bio-degrade in living systems. The implication of this is that they accumulate in living systems, eventually causing serious health hazards to the ecosystem in general. In most cases, these metals, like mercury (Hg) and Copper (Cu), occur naturally in the soil. [1, 2] In the last two decades, the concerns about heavy metal toxicity have significantly increased, as they have continued to cause havoc in living systems. Cadmium (Cd), for example, can accumulate in the kidney and liver for over ten years and affect physiological functions in the body. [3, 8] This necessitates the need for various methods for the removal of heavy metals from the body. The current methods of heavy metal removal like electro-coagulation are too expensive, require technical expertise, and end up constituting more biological damage to the ecosystem.[4, 10] This is why there is a need for a cost-effective and safe procedure for heavy metal removal like bio-sorption.

Bio-sorption has numerous advantages over conventional methods of heavy metal removal including low cost, high efficiency, the possibility of metal recovery, and minimization of chemical or biological sludge, amongst others. [4] The bio-sorption process involves a solid phase (sorbent or bio-sorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be adsorbed (sorbate, metal ions). Due to the higher affinity of the sorbent for the sorbate species, the latter is attracted and bound, by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and the portion remaining in the solution. [5]

This study shows the feasibility of using jackfruit seeds for the adsorption of heavy metals mixture of lead, cadmium, and arsenic from solution using an atomic adsorption spectrometer. The Jackfruit (*Artocarpus heterophyllus*), also known as the Jack tree, is a tree in the fig, mulberry, and breadfruit family (Moraceae). Jackfruit seeds have been investigated for the removal of heavy metals from the solution. Prasad et al., reported that the presence of the carboxyl group in jackfruit seed plays a significant role in eliminating Cadmium from the solution. [6] The company of polar groups on the bio-sorbent surface provided considerable cation exchange capacity to the adsorbent. [7, 9] Zahrim et al., also reported that results from an experiment using jackfruit seeds as an adsorbent for removing ammonia nitrogen from aqueous solution through batch and column methods prove jackfruit seed to be a promising adsorbent in removing ammonia nitrogen from solution. [7, 11]

2. Materials and Method

Jackfruit was bought from a local market in Kogi state, Nigeria. The fruits selected were ripe. The fruit was cut open, and the seed was separated from the flesh. The fresh seed was manually decorticated, cleaned, and their white aril peeled off. The seed was washed with water to remove dirt and sand, then dried at room temperature. The properly dried sample was then pulverized using mortar and pestle as the seeds were too tough to grind using a blender at the initial stage. After the initial particle size reduction was achieved, a blender was used to reduce the seed sample. The sample was then sieved using sieves with mesh sizes 2000µm, 425µm, and 850µm, the materials that passed through each sieve size were collected and placed in individual closed containers and properly labeled.

Preparation of the stock solution for the lead was done by weighing 200mg of lead nitrate and placing it in a conical flask. 100ml distilled water was added to it and stirred. From this mixture, 10ml was obtained, which contained 20mg of lead nitrate, placed in a 1000ml measuring cylinder, and distilled water was added to make the mixture up to 1000ml.

The same procedure was carried out with 160mg of cadmium chloride and 100mg of arsenic oxide.

The final concentration used was 0.02mg/L, 0.016mg/L, and 0.01mg/L for lead nitrate, cadmium chloride, and arsenic oxide respectively.

10ml of lead nitrate solution, 10ml of arsenic oxide solution, and 1ml of cadmium chloride solution were withdrawn from their respective stock solutions and transferred into a 1000ml measuring cylinder. Distilled water was added to make up to 1000ml volume, and the mixture was transferred into a 1000ml conical flask. The pH of the metal mixture was checked and kept at 5.5.

The following procedures outlined by Abdel Salam et al., (2011) were adopted to determine the adsorption capacity of the bio-sorbent.

After sieving, 1g of particle sizes 425µm, 850µm, and 2000µm of jackfruit seed was placed in three (3) conical flasks, respectively, and 100 ml of the heavy metal mixture used was added to each conical flask. The same procedure was replicated using 5 grams of Jackfruit seed powder.

All experimental mixtures containing adsorbent (Jackfruit seed) and the ad-sorbate (metal solutions) were placed on an electrical shaker. The rotation speed of the shaker was set to 90 cycles per minute. After one (1) hour, the shaker was stopped, and 5 ml filtrate was removed from each mixture using a Whatman No 1 filter paper, and the shaking was continued for another two (2) hours.

At the end of 3 hours of contact time, another 5 ml of filtrate was removed using a Whatman No 1 filter paper. The filtrates were placed in sample collection bottles, labelled blindly, and analysed using Atomic Absorption Spectrometer (AAS) to determine the final concentration of heavy metals in the filtrate of the samples collected.

3. Results

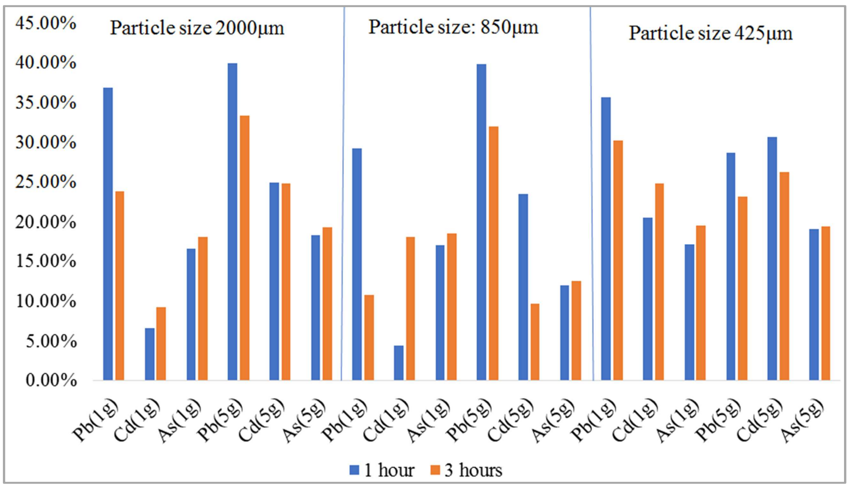

Figure 1. *Percentage (%) adsorbance of lead, arsenic, and cadmium in a mixture by 1g and 5g doses of jackfruit seed of particle sizes 2000µm, 850µm, and 425µm at 1 hour and 3 hours contact time.*

Figure 1 shows the rate of adsorption of varying doses of jackfruit seed at varying particle sizes after one and three hours of contact time. At 2000µm, after one hour of contact time, 1g of Lead, Arsenic, and Cadmium had a percentage adsorbance of 36.91%, 16.61%, and 6.66%, respectively. But after 3 hours, % adsorption became 23.80%, 18.16%, and 9.28% for lead, arsenic, and cadmium respectively. This revealed that adsorption reduced with time for lead, but arsenic and cadmium had increased adsorption with the prolonged time. As for the 5g dose, after one hour of contact time, lead, arsenic, and cadmium had a percentage adsorbance of 39.96%, 18.31%, and 24.98%, respectively. And after 3 hours of contact time, adsorption reduced with time for lead and cadmium, but arsenic had increased adsorption with the prolonged time.

With a change in particle size, there was also a change in the level of adsorption. For 1g of particle size 850µm, after one hour of contact time, Lead, Arsenic, and Cadmium had a percentage adsorbance of 29.24%, 16.98%, and 4.38%, respectively. But after 3 hours of contact time, % adsorbance changed. Adsorption of lead reduced with time but arsenic and cadmium showed increased adsorption after 3 hours of contact time. When the dose was increased to 5g, adsorbance for the first hour was 39.88%, 11.94%, and 23.54% for lead, arsenic, and cadmium, respectively. At the third hour, lead still had the highest adsorption rate, but adsorbance for arsenic was higher than cadmium. This shows that desorption occurred sometime before the third hour for lead and cadmium. It could be such that as time progressed, the surface of the adsorbent could no longer adsorb more particles, and as more time passed, under consistent shaking, it began to lose some metal ions. Arsenic had a favourable adsorption rate in the metal mixture as adsorption continued to increase up until the third hour.

For the particle size 425µm, after one hour of contact time, Lead, Arsenic, and Cadmium had a percentage adsorbance of 35,64%, 17.12%, and 20.51%, respectively but at the third hour, lead's adsorption reduced with time while the other metals increased. At 5g dose of jackfruit seed, one hour of contact time yielded adsorption percentage of 28.66%, 19.10%, and 30.61%, respectively for Lead, Arsenic, and Cadmium. After 3 hours, adsorbance reduced for lead and cadmium, but arsenic had a slight increase in adsorption with the prolonged time.

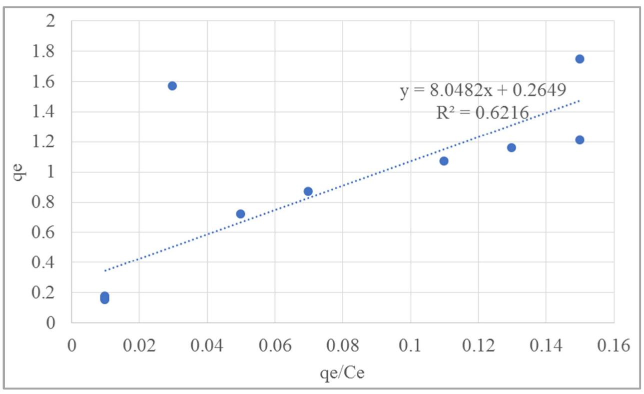

Figure 2. *Langmuir adsorption isotherm plot for adsorption of lead ions from metal mixture using jackfruit seed as bio-sorbent.*

Table 1. *Isotherm parameter for the removal of Lead by jackfruit seed.*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Langmuir model	Adsorption constant	0.12
	Adsorption capacity Qmax	0.2649
	Correlation Coefficient R^2	0.6216
	Regression Equation	Y=8.04824 x 0.2649

Figure 2 and table 1 show the Langmuir adsorption isotherm for lead ions in the metal mixture. From the graph plotted, the values of adsorption constant, adsorption capacity and correlation coefficient which were 0.12, 0.2649 and 0.6216 respectively, were obtained. The adsorption capacity was less than one which showed that adsorption was favourable.

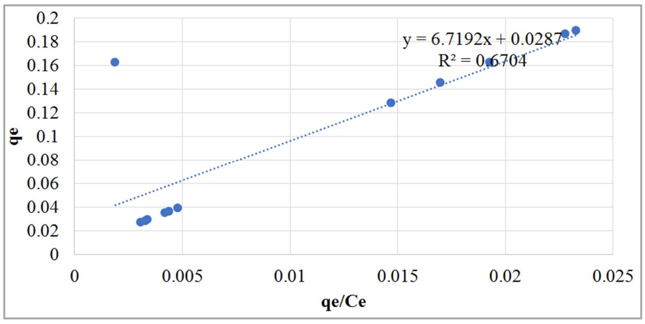

Figure 3. *Langmuir adsorption isotherm plot for adsorption of arsenic ions from metal mixture using jackfruit seed as bio-sorbent.*

Table 2. *Isotherm parameter for the removal of Arsenic by jackfruit seed.*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Langmuir model 3	Adsorption constant	0.19
	Adsorption capacity Qmax	0.0287
	Correlation Coefficient R^2	0.6704
	Regression Equation	Y=6.7192x + 0.0287

Figure 3 and table 2 show the Langmuir adsorption isotherm for arsenic ions in the metal mixture. From the graph plotted, the values of adsorption constant, adsorption capacity and correlation coefficient which were 0.19, 0.0287 and 0.6704 respectively, were obtained. The adsorption capacity was less than one which showed that adsorption was favourable.

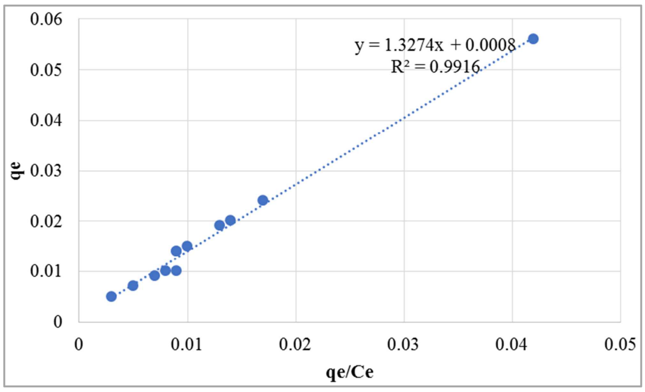

Figure 4. *Langmuir adsorption isotherm plot for adsorption of cadmium ions from metal mixture using jackfruit seed as bio-sorbent.*

Table 3. *Isotherm parameter for the removal of Cadmium by jackfruit seed.*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Langmuir model 3	Adsorption constant	0.75
	Adsorption capacity Qmax	0.0008
	Correlation Coefficient R^2	0.9915
	Regression Equation	Y= 1.3744x + 0.0008

Figure 4 and table 3 show the Langmuir adsorption isotherm for cadmium ions in the metal mixture. From the graph plotted, the values of adsorption constant, adsorption capacity and correlation coefficient which were 0.75, 0.0008 and 0.9915 respectively, were obtained. The adsorption capacity was less than one which showed that adsorption was favourable.

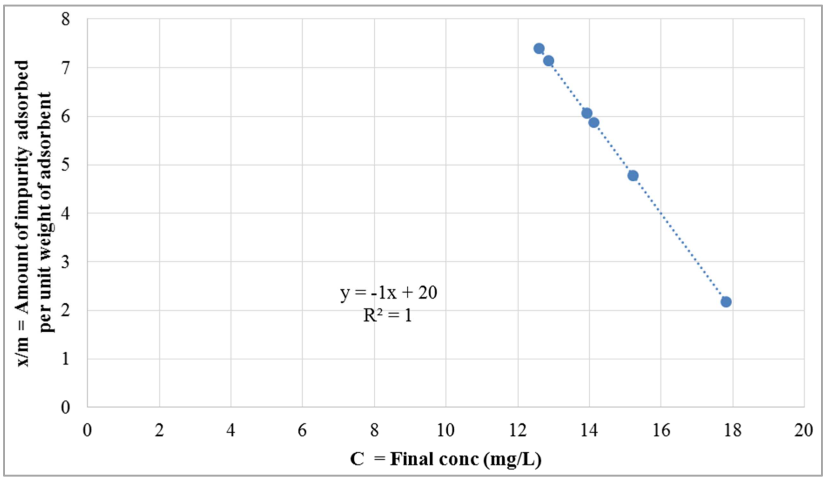

Figure 5. *Freundlich adsorption isotherm for adsorption of lead on jackfruit seed (1g).*

Table 4. *Isotherm parameter for the removal of Lead by jackfruit seed (1g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	1
	Adsorption capacity Qmax	20
	Correlation Coefficient R^2	1
	Regression Equation	y = -1x + 20

Figure 5 and table 4 show that 1/n is equal to one which means that the rate of adsorption is dependent on concentration. So at this point, adsorption could change as concentration changes.

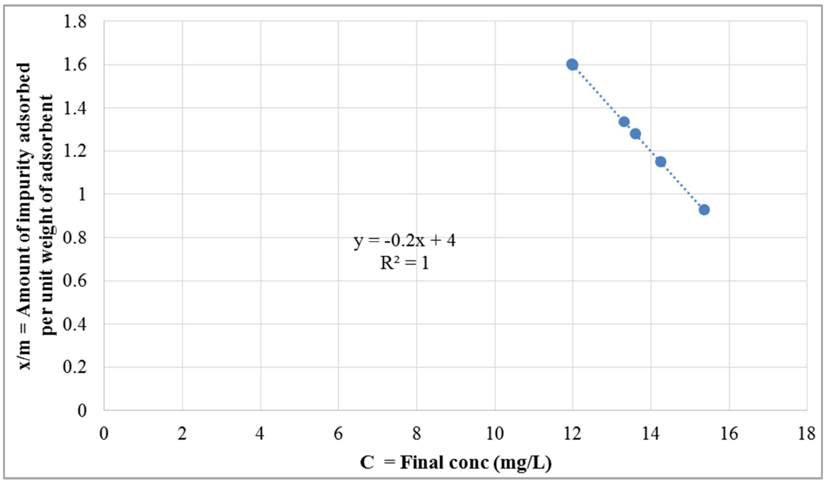

Figure 6. *Freundlich adsorption isotherm for adsorption of lead on jackfruit seed (5g).*

Table 5. *Isotherm parameter for the removal of Lead by jackfruit seed (5g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	0.2
	Adsorption capacity Qmax	4
	Correlation Coefficient R^2	1
	Regression Equation	y = -0.2x + 4

Figure 6 and table 5 shows the Freundlich isotherm for the adsorption of lead onto 5g of jackfruit seed from the metal mixture. The table shows that 1/n is equal to 0.2, which means that adsorption at this point is independent of the concentration of the jackfruit seed.

Table 6. *Isotherm parameter for the removal of Arsenic by jackfruit seed (1g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	1
	Adsorption capacity Qmax	10
	Correlation Coefficient R^2	1
	Regression Equation	y = -1x + 10

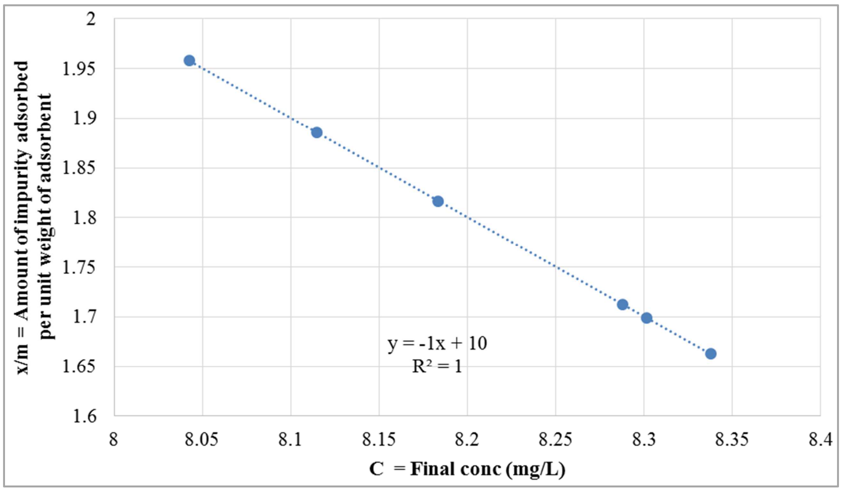

Figure 7. *Freundlich adsorption isotherm for adsorption of Arsenic on jackfruit seed (1g).*

Figure 7 and table 6 show that 1/n is equal to one for the adsorption of arsenic unto 1g of Jackfruit seed. This shows that the rate of adsorption is dependent on concentration. So at this point, adsorption could change as concentration changes.

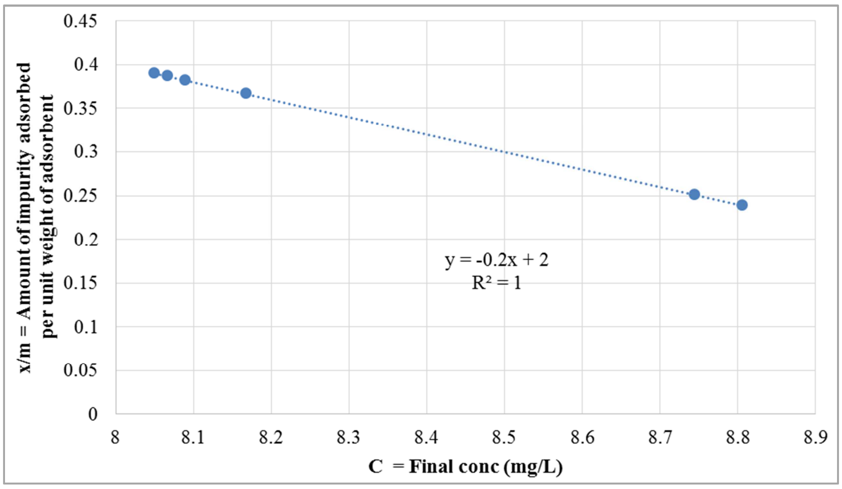

Figure 8. *Freundlich adsorption isotherm for adsorption of Arsenic on jackfruit seed (5g).*

Table 7. *Isotherm parameter for the removal of Arsenic by jackfruit seed (5g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	0.2
	Adsorption capacity Qmax	2
	Correlation Coefficient R^2	1
	Regression Equation	y = -0.2x + 2

Figure 8 and table 7 shows the Freundlich isotherm for the adsorption of arsenic onto 5g of jackfruit seed from the metal mixture. The table shows that 1/n is equal to 0.2, which means that adsorption at this point is independent of the concentration of the jackfruit seed.

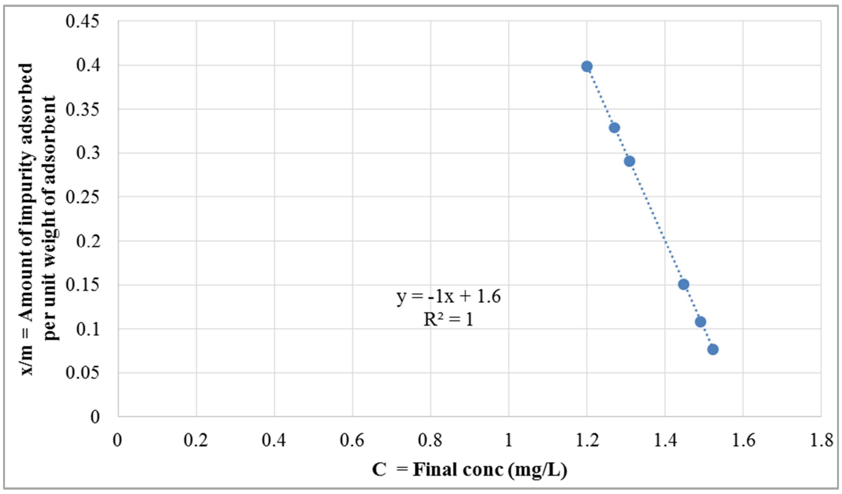

Figure 9. *Freundlich adsorption isotherm for adsorption of Cadmium on jackfruit seed (1g).*

Table 8. *Isotherm parameter for the removal of Cadmium by jackfruit seed (1g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	1
	Adsorption capacity Qmax	1.6
	Correlation Coefficient R^2	1
	Regression Equation	y = -1x + 1.6

Figure 9 and table 8 show that 1/n is equal to 1 for the adsorption of cadmium on 1g of jackfruit seed. This shows that the rate of adsorption is dependent on concentration. So at this point, adsorption could change as concentration changes.

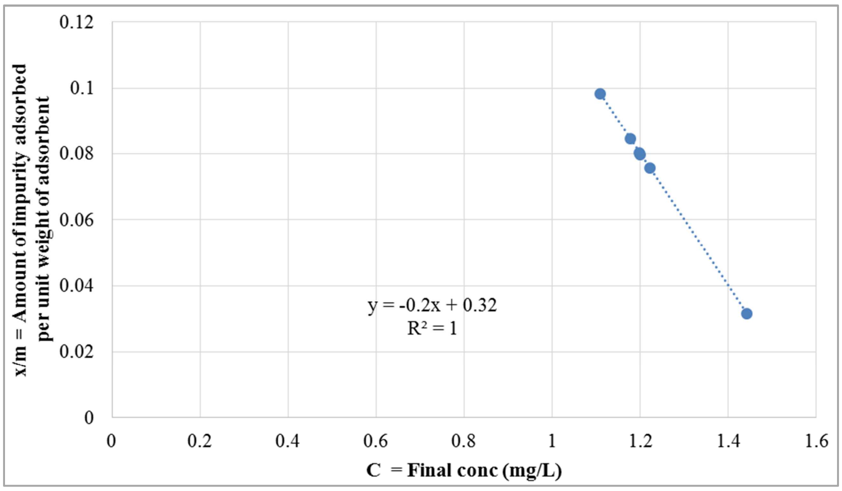

Figure 10. *Freundlich adsorption isotherm for adsorption of Cadmium on jackfruit seed (5g).*

Table 9. *Isotherm parameter for the removal of Cadmium by jackfruit seed (5g).*

ISOTHERM MODEL	PARAMETER	JACKFRUIT SEED
Freundlich	1/n	0.2
	Adsorption capacity Qmax	0.32
	Correlation Coefficient R^2	1
	Regression Equation	y = -0.2x + 0.32

Figure 10 and table 9 shows the Freundlich isotherm for the adsorption of Cadmium onto 5g of jackfruit seed from the metal mixture. The table shows that 1/n is equal to 0.32, which means that adsorption at this point is independent of the concentration of the jackfruit seed.

4. Discussion

The results obtained show the amount of heavy metal adsorbed by jack fruit seed when adsorbent dose, contact time, and particle size vary. The results showed that lead was most adsorbed, followed by arsenic and cadmium, respectively (Pb> As> Cd) from the metal mixture. The adsorption was also plotted by using the isotherm parameters of Langmuir equations.

The profile obtained from the study of concentration at different doses was used to obtain Langmuir and adsorption isotherms by using well-known adsorption isotherm equations. The linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. The results that the adsorption kinetics followed the Langmuir adsorption of heavy metals.

Adsorption constant in the Langmuir graph is the criteria used to show the affinity between the adsorbent and adsorbate particles. The higher the magnitude of the constant, the stronger the interaction between the molecules and if the constant is smaller, the interaction is weak. Adsorption is said to be irreversible regression factor is equal to zero, and if it is less than one, adsorption is favourable. A value greater than one means that adsorption is unfavourable. According to the results obtained from the Langmuir graph, adsorption was favourable to all the metal ions and the adsorption is reversible as the regression factor is less than one in every graph.

For the Freundlich adsorption isotherms, the value of 1/n varies from 0 to 1. If 1/n is 0, adsorption is independent of concentration. If 1/n is 1, adsorption changes with concentration. The graph is plotted according to the concentration of adsorbent and the results show that rate of adsorption at lower doses of adsorbent (1g) are dependent on concentration while higher doses (5g) are independent of concentration.

Contamination by heavy metals usually occurs in a mixture and not singly. At an adsorbent dose of 1g and 5g, the percentage adsorbance of lead ions in the metal mixture by jackfruit seed reduced with time. As time progressed, the surface coverage of the adsorbent became high, and no further adsorption took place, all in three hours. This behaviour could be a result of lead physiochemical properties. The mass of the jackfruit powder used did not appreciably affect its absorbance of lead as the variations showed little correlation.

Summarily, particle sizes 2000µm yielded more absorbance than that of 850µm, followed by 425µm. Also, this is attributed to the surface phenomenon of adsorption wherein more finely divided particles allow more surface area and, as a result, more adsorption.

For arsenic, the percentage adsorbance of metal ions by jackfruit increased with time. The mass of the jackfruit powder used did not affect its adsorbance of arsenic. There was no significant increase or decrease in arsenic adsorption following the mass change.

The results showed that particle size 425µm usually yielded more adsorbance of arsenic ions than particle sizes 2000µm and 850µm. Our study is in line with the reports of Khan et al., stating that adsorption is a surface phenomenon, and more finely divided particles mean more surface area and, as a result, more adsorption. [12- 15]

In the adsorption of Cadmium in the metal mixture, the percentage adsorbance of the metal ions by Jackfruit seed reduced with time at a higher adsorbent dose but increased with time at a lower dose. Generally, with an increase in the amount of adsorbent in the solution, the rate of adsorption of the adsorbate is also increased due to the rise in the number of available active sites on the adsorbent. [16-19]

Our study also agrees with Prasad et al., which say a lesser mass of 600mg yielded maximum adsorption, and a further increase in mass-produced no significant increase in adsorption. [6]

5. Conclusion

The present study shows the capability and effectiveness of jackfruit seed as a biosorbent for removing lead, arsenic, and cadmium from a metal mixture at varying doses, particle sizes, and contact time. The results showed that jackfruit seed has great potential in the adsorption of heavy metals and is a preferred method of eliminating heavy metals as it is environmentally friendly, easily accessible, gotten at little or no cost, and further studies can also be carried out for the desorption of the heavy metals from the adsorbent, completely eliminating waste, which places it above other conventional methods of elimination of heavy metals from the environment.

Declarations

Ethical Approval

This article does not require ethical approval as it did not involve studies on humans or animals.

Consent for Publication

Not applicable.

Availability of Data and Materials

The data and materials are available at Madonna University Pharmacology laboratory.

Competing Interests

There are no relevant financial or non-financial competing interests to report for this article.

Author's Contribution

OVB: Conceptualizing the topic, conducting literature review, writing the manuscript, and finding the right journal. ZNI: Conceptualizing the topic and Reviewing the manuscript. HCO: Reviewing and revising the manuscript.

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