**Poll Res. 44 (3–4) : 210-219 (2025)**
Copyright © EM International
ISSN 0257–8050

**DOI No.: http://doi.org/10.53550/PR.2025.v44i03-04.010**
**Journal Home Page:** www.envirobiotechjournals.com

# CHARACTERIZATION AND ADSORPTION ISOTHERMS FOR THE BIOREMEDIATION OF CU AND ZN IONS FROM AQUEOUS SOLUTIONS USING ARECANUT HUSK

**GURUPRASHANTH N.[1], UDAYAKUMAR G.[2] AND SURESH B.[3]**

*[1]Department of Civil Engineering, Srinivas University, Institute of Engineering and Technology, Mukka, Mangalore and Department of Civil Engineering, Jain Institute of Technology, Davangere 577 004, India*
*[2]Department of Civil Engineering, Srinivas University, Institute of Engineering and Technology, Mukka, Mangalore, India*
*[3]Department of Civil Engineering, Bapuji Institute of Engineering and Technology, Davangere 577004, Karnataka, India*

(Received 24 January, 2025; Accepted 12 March, 2025)

## ABSTRACT

**Environment is contaminated by heavy-metals has emerged as a substantial global concern. Conventional remediation methods have proven inadequate and costly in addressing this issue. Hence, there is a pressing need to explore bioremediation as a cost-effective, efficient, and environmental friendly, an alternative for heavy- metal removal. This study investigates the adsorption behaviour of Arecanut Husk (AH), an inexpensive adsorbent, towards Cu and Zn ions for potential application in wastewater treatment. The physicochemical properties of unmodified Arecanut Husk were appraised, and batch experimental methods were employed to study variables such as pH, contact-time, particle size, initial content of metal. The impact of solution pH on metal ion uptake by the adsorbent was investigated on the pH range of 3 to 8, revealing optimal removal efficiencies at pH 6 for Cu and pH 5 for Zn. Equilibrium adsorption times were determined to be 80 minutes for Cu and 60 minutes for Zn ions onto Arecanut Husk. Adsorption capacities is corresponding to monolayer coverage, attained from the Langmuir plots were 4.792 mg/g and 4.594 mg/g correspondingly for Cu and Zn ions onto the Arecanut Husk. Experimental results were confirmed to the Langmuir and Freundlich models, with the Langmuir model providing the best fit. The Arecanut Husk based adsorbent was generally found to have an increased capacity of adsorption of the metal ions. These findings underscore the potential of Arecanut Husk as an active adsorbent to remove cationic heavy-metal contents from industrial wastewater.**

**KEY WORDS:** Bio-sorbents, Adsorption Isotherm, Model, Arecanut Husk

## INTRODUCTION

**Abbreviations:** AH: Arecanut Husk

The contamination of the environment through the exhaust of toxic substances in wastewater is an important issue affecting both public health and environmental well-being. Among trace pollutants, heavy-metals stand out as particularly hazardous (Tchuifon, *et al.,* 2014 and Otitoju and Gto Otitoju, 2013). Their presence has tainted numerous bodies of water, posing risks to human-health and other living organisms. The release of heavy-metals poses a considerable threat due to their toxicity, tendency

[1]ORCID-ID : 0000-0002-7316-4896
[2]ORCID-ID: 0009-0006-2304-493X
[3]ORCID-ID : 0000-0001-7482-6487

to accumulate in the food chain, and long-lasting influence on the environment (Song, *et al.,* 2013; Igwe, *et al.,* 2007; Otitoju, 2012;Hossain and Rahman, 2012). Studies indicate that the toxicity resulting from metallic pollutants surpasses that of combined radioactive and organic waste (Otitoju, 2012; Veglio and Beolchini, 1997). Additionally, these pollutants can contribute to an increase in nutrient levels in water bodies, particularly if some essential metals (Kehinde, *et al.,* 2009). Furthermore, heavy-metals in wastewater can increase the fertility of sediment and water columns, leading to eutrophication. This process, especially prevalent in open waters, can ultimately lead to oxygen depletion, algal blooms, and the demise of aquatic life (Song, *et al.,* 2013; Veglio and Beolchini, 1997; Otitoju and GtoOtitoju, 2013 and Igwe, *et al.,* 2007).

Consequently, the management of waste-water polluted with heavy-metals remains a global concern as it is sourced from municipalities, communities, and industries and must eventually be reintroduced into receiving waters or the land (Deepa, 2006 and Badmus, 2007). Traditional treatment approaches have proven to be costly and challenging to sustain due to their capital and operational expenses, leading to the production of chemical sludge and secondary waste that requires treatment prior to disposal, posing environmental hazards and risks (Argun and Dursun, 2006; Weber, 1991; Asamudo, 2005 and Viraraghavan and Dronamraju, 1993). These boundaries have prompted interest and research into more well-organized and environmental friendly methods (Reed, 1994 and Rangel, 2012)for heavy metal treatment, such as adsorption. Adsorption involves utilizing inexpensive, naturally occurring organic and waste materials from agricultural practices as adsorbents, which have been documented in numerous studies as effective in treating metal-contaminated wastewater (Reed, 1994 and Rangel, 2012). The benefits of adsorption contain its cost-effectiveness, high efficacy, decreased in production of chemical and biological sludge, potential for adsorbent regeneration, and recovery of metal (Volesky, 1994 and Kumar, 2006). The accumulation of biomass in the ecosystem due to its disposal as waste following high consumption rates has raised environmental concerns regarding land occupation and subsequent pollution issues. Therefore, this paper explores the potential application of recycled AH agro-waste in the remediation of Cu and Zn ion-contaminated wastewater through the adsorption phenomenon as a substitute for the treatment approach (Okieimen, 1991; Abia, 2003; Sajidu, 2006; Ong, 2007; Argun, 2007; Bansal, 2009; Nharingo and Hunga, 2013; Nharingo and Hunga, 2013; Dawodu, *et al.,* 2014 and Kumar and Gayathri, 2009).

## MATERIALS AND METHODS

### Adsorbent

The Arecanut Husk (AH) was sourced from a local agricultural land in agricultural land outside Davangere city in Karnataka State, India. Sample materials underwent a rigorous cleaning process involving tap water and subsequent wetting with double distilled water to remove surface dust and impurities. Following this, the husks were air-dried and dehydrated in an oven at 80°C until a consistent mass was achieved. The dried bio-mass was milled and sieved through an electromagnetic sieve to attain particle sizes smaller than 250 µm. Finally, the dried bio-mass was stored in airtight polyethylene bags to control it from moisture and prepare it for appraisal (Qaiser, 2009; Kumar and Bandyopadhyay, 2006 and Khan and Wahab, 2006). Its significant to reminder that the adsorbent was used in its natural condition without any modifications.

### Preparation of stock solutions

Analytical grade chemicals were employed in the preparation of all solutions utilized in the study. A synthetic stock solution of Cu and Zn (1000 mg/l) was created by dissolving 2.51 g of $CuSO_4$ and 0.44 g of $ZnSO_4$ separately in 1000 ml of double distilled water. Subsequent concentrations of the trace-metal ions were achieved through serial dilution from the stock solutions. The pH of the aqueous solutions was adjusted using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide (Shukla and Pai, 2005a and Shukla and Pai, 2005b).

### Moisture Content

The determination of moisture content involved placing 5 g of the substance (AH) into a separate crucible, followed by heating it in an oven for a consistent 5-hour period at 105°C. After heating, the sample was promptly transferred to a desiccator to prevent moisture absorption from the surrounding atmosphere. Subsequently, the sample was re-weighed, and this phenomenon was repeated multiple times until a consistent weight was achieved. The variance in mass after heating

represents the moisture content in the adsorbents (AH), which was noted as 23% and 24% respectively. Moisture content is determined using the equation below.

$$\%\text{Moisture content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad .. (1)$$

$W_1$ = weight of crucible
$W_2$ = Initial weight of sample
$W_3$ = Final weight of sample

**Loss of mass**

The process of determining the loss of mass upon ignition involved initially weighing 10g of the adsorbent (comprising AH) and placing it in a furnace set at a consistent temperature of 580°C for duration of 2 hours. Following the heating process, the sample was taken out and allowed to cool within a desiccator. The remaining product was subsequently weighed, with the variance in mass indicating the quantity of organic-material within the sample. This series of steps was repeatedly done for four times to get accuracy and reliability.

**Bulk density**

The bulk density of AH samples was evaluated using Archimedes principle. Initially, a 10cm³ measuring container was taken and filled with the samples to determine their mass. Afterwards, the measuring container was dried, and the sample was carefully packed inside and reweighed. The weight of each sample crowded in the measuring cylinder was estimated by the loss in weight between the filled and empty measuring cylinder. The total volume of water displaced by the sample was estimated by measuring the weight difference between the empty and water-filled measuring cylinder. Finally, the bulk-density was estimated using the equation below (Dada, 2012).

$$\text{Bulk Density} = \frac{W_2 - W_1}{V} \quad .. (2)$$

**Batch Equilibrium adsorption Studies**

Batch equilibrium adsorption study was conducted using 100 ml plastic bottles following the procedures outlined by Nharingo and Hunga, (2012) and Dawodu and Kovo, (2014). These experiments aimed to examine the impact of key experimental variables on the adsorption phenomenon. The critical variables scrutinized in this investigation included pH, contact-time, dosage, particle-size, and initial metal contents. To maintain consistency, solution temperature, volume of synthetic effluent, and agitation rate were kept constant at 25±2°C, 50 ml and 180 rpm respectively, throughout 120-minute study duration.

**Effect of adsorbents dosage on adsorption**

In individual 50 ml aliquots of solutions containing Cu and Zn ions at a concentration of 200 mg/l, biomass quantities ranging between 0.1 g and 1 g were added to 100 ml plastic containers. The solutions were then agitated applying 180 rpm in a shaker for 120 minutes at 25±2 °C temperature of and a 6.0 pH. Subsequently, the mixtures underwent filtration, and the residual metal ions were appraised using an atomic absorption spectrophotometer (AAS) (Buck Scientific, model 210VGP).

**Effect of pH on adsorption**

The impact of pH on the removal percentage of Cu and Zn ions by AH was explored using initial aqueous solutions containing 200 mg/l of Cu and Zn ions. Each 100 ml plastic bottle received in different volumes of 50 ml of the 200 mg/l Cu and Zn ion solutions. pH adjustments were made within the range of 3.0 to 8.0 using 0.1 M HCl and 0.1 M NaOH solutions. Subsequently, 1g of AH were individually added to each plastic bottle consisting metal solutions with varying pH. The mixtures then placed on an electric shaker operating at 180 rpm for 120 minutes at a temperature of 25±2 °C. Finally, the samples were cleaned and subjected to analysis for residual metal-ions (Yang, *et al.,* 2011 and Wang, *et al.,* 2009).

**Effect of initial metal concentrations on adsorption**

The impact of initial contents of metal-ions on adsorption was investigated under optimal conditions. This involved blending 1 g of AH powder with 50 ml of solutions containing Cu and Zn ions with changing initial concentrations ranging from 50 to 200 mg per liter at a pH of 6.0. The experiments were carried out at a controlled temperature of 25 ± 1 °C with a shaking rate of 180 rpm for duration of 120 minutes (Das and Mondal, 2011 and Barka, 2013). Subsequently, the samples were filtered and appraised for residual metal-ions using an atomic absorption spectrophotometer (AAS).

**Effect of contact time on adsorption**

Batch adsorption setups were carried out over

various contact durations ranging from 5 to 120 minutes. Each experiment involved mixing 50 ml of a solution containing Cu and Zn ions at a concentration of 200 mg/l with 1.0g of adsorbent at a pH of 6.0. The mixtures were agitated in flasks at a rate of 180 rpm and maintained at room temperature 25±2 °C. The concentration of residual metal-ions was appraised at predetermined intervals using an AAS. The equilibrium times were determined to be 30 minutes for Cu and 60 minutes for Zn. Consequently, a contact time for 120 minutes was selected for subsequent experiments to ensure attainment of equilibrium conditions (Das and Mondal, 2011).

**Effect of adsorbent particle sizes on adsorption**

Each 50 ml portion of a solution containing Cu and Zn ions at a concentration of 200 mg/l was placed in separate 100 ml plastic containers. Biomass particles ranging in size from 1000 to less than 250ìm were added to each bottle individually. The mixtures were then agitated on a shaker at 180 rpm for 120 minutes at a temperature of 25±2 ºC and a pH of 6.0. After agitation, the mixtures were filtered, and the residual metal ions were appraised using an AAS Throughout the experiments, one variable was changed while the others remained constant (Amuda and Ibrahim, 2006 and Yao, *et al.*, 2009). Filtration occurred at the conclusion of each specified contact time, and the concentration of metal ions remaining in the filtrate was determined using the same AAS. Each setup was repeated twice, and the mean value was calculated to minimize error. The quantity of metal-ions adsorbed per-unit-mass of the adsorbent was determined using equations 3 and 4 (Kumar and Gayathri, 2009).

$$Q = \frac{V(C_i - C_e)}{W} \quad .. (3)$$

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad .. (4)$$

Q = the amount of solute adsorbed from the solution

V = Volume of the adsorbate

$C_1$= the concentration before adsorption

$C_e$ = the concentration at equilibrium and

W = the weight in g of adsorbent

The efficiency of removal was assessed by calculating the percentage of sorption, as outlined in Equation (4) (Igwe, 2005).

## RESULTS AND DISCUSSION

**Fourier transforms infrared spectroscopy (FTIR) analysis**

The surface a characteristic of the bio-sorbents AH isinvestigated through FT-IR spectroscopy as presented in Figure 1. Analysis of the spectra revealed several absorption peaks, indicative of various functional groups present on these bio-sorbents, potentially involved in the removal of metal-ions from aqueous solutions. For CH peaks were observed at 3461.38 cm-1 (N-H stretch), 1640.51 cm-1 (C = C bond), and 1192.05 cm-1 (C-O stretch), AH exhibited peaks at 3440.16 cm-1 and various other wavelengths corresponding to different functional groups. Notably, the presence of N-H stretch, C = C bond, C-O stretch, N-H bend, and C-H bend suggests potential sites for adsorption of Cu and Zn ions. These functional groups, possessing either ð-electrons or lone pairs on nitrogen or oxygen, can mix with metal ions, facilitating adsorption. Comparison of spectra suggests surface variations possibly due to carbonization of bamboo waste, leading to the emergence of new peaks or absence of certain ones.

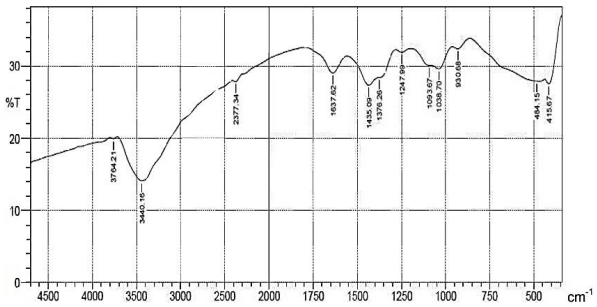


**Fig. 1.** FTIR spectra of Arecanut Husk before adsorption

**Effect of pH**

The pH of a solution is a key and crucial role in the adsorption of metals from aqueous solutions. It affects the binding locations on the adsorbent surface and the chemistry of metals in the solution. In the current study, we estimated how pH influences the adsorption of Cu and Zn ions by two different adsorbents within the pH range of 2.0 to 6.0, as depicted in Figure 2. This paper did not explore pH values beyond 6.0 to prevent the precipitation of Zn and Cu as hydroxides. The results of the tests indicate that the maximum adsorption of Cu and Zn on selected adsorbents occurred at pH 6.0. At lower pH levels, competition

between metal ions and hydronium ions for active locations on the adsorbent surface led to lower metal uptake. Previous research has reported that in highly acidic conditions, the adsorbent surface ligands may closely associate with hydronium ions, hindering the access of metal ions due to repulsive forces. Therefore, as pH increases, more ligands are exposed, leading to the attraction of positively charged metal ions.

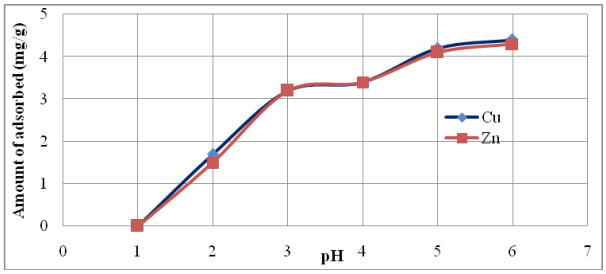


**Fig. 2.** Effect of pH on Cu and Zn adsorption onto AH

### Impact of initial metal ion concentration

Figure 3 illustrate that as the concentration of metal-ions increased, their adsorption onto the adsorbents also increased. Evaluating the level of metal-ion uptake revealed that Cu ions exhibited slightly superior adsorption compared to Zn ions on adsorbent. The absence of flattening in the curves even at the highest initial content of 100 mg/l, as utilized in our investigation, suggests an incomplete occupation of the available adsorption sites by the metal ions. Furthermore, the augmentation in adsorption with rising initial concentration is corroborated by the distribution coefficients provided in Table 1. These coefficients, representing the ratio of metal-ion concentration in the adsorbent phase to that in the continuous phase, delineate the relative efficiency of the adsorbents in binding the metal ions. Notably, all distribution coefficients in Table 1 exceeded unity for the initial metal ion concentrations employed, signifying an uptake of more than 50%. However, as the initial concentration of metal ions increased, the distribution co-efficient generally declined.Once again, the observation stands that Cu, characterized by its larger density and higher ionic radius as illustrated in Table 2, exhibited superior adsorption compared to Zn. This phenomenon can be rationalized by the tendency of metal ions to form aquo complexes upon dissolution in water (Abia, 2022).

**Table 1.** Distribution coefficients for adsorption of the Cu and Zn metal ions

| Initial Conc. (C0) (mg/l) | AH | |
|---|---|---|
| | Cu | Zn |
| 20 | 42.41 | 25.79 |
| 40 | 12.72 | 11.42 |
| 60 | 12.56 | 11.46 |
| 80 | 5.99 | 4.05 |
| 100 | 4.28 | 3.74 |

The aquo complex is of the form $[M(H_2O)_x]^{n+}$ where 'M' represents the metal ion, 'n+' denotes the net charge on the complex, and 'x' signifies the coordination number. The comparative uptake levels of these metal ions are inversely proportionated with their respective hydration energies, as indicated in Table 2. Specifically, Zn with an ionic radius of 0.097 nm possesses hydration energy of -1806 kJ/mol, whereas Cu with an ionic radius of 0.12 nm exhibits hydration energy of -1480 kJ/mol. Given that the displacement of water molecules from the aquo ion underpins adsorption dynamics, the stability of the aquo ion emerges as a significant factor in the adsorption process. The stability of the aquo ion, as evidenced by the hydration energies of the metal ions, is contingent upon the ion's size. Notably, ions with relatively larger sizes (and lower hydration energies) display weaker relations with water molecules compared to ions with smaller sizes (and relatively higher hydration energies). Consequently, ions with greater sizes are more adept at interacting with adsorbents since they can more-readily displace the water molecules from the aquo complex. This mechanism likely contributes to the enhanced adsorption of Cu ions over Zn ions.

However, it was noticed that the percentage of Cu and Zn ions adsorbed from the solution decreased as the initial metal-ion concentration enhanced for adsorbent as presented in Figure 4.

**Table 2.** Physical and Chemical properties of Cu and Zn ion metals

| Element | Stable oxidation states | Density g/cm$^3$ (25 $^0$C) | Ionic radii (À) | Hydration energy (ΔH) kJ/mol |
|---|---|---|---|---|
| Copper | +1 and +2 | 8.96 | 0.73 | -78.20 |
| Zinc | +2 | 7.14 | 0.79 | -2049 |

This phenomenon occurs because at lower metal ion concentrations, nearly all the metal ions are adsorbed. However, as the initial concentrations of metal-ions increase, the ratio of metal ions to available surface active sites also increases. Consequently, fractional adsorption becomes more dependent on the initial concentration. Despite a constant dose (mass) of the adsorbent, the total available adsorption sites are limited, leading to the adsorption of a similar amount of metal ions. This ultimately results in decreased removal efficiencies of the metal-ions by the adsorbent

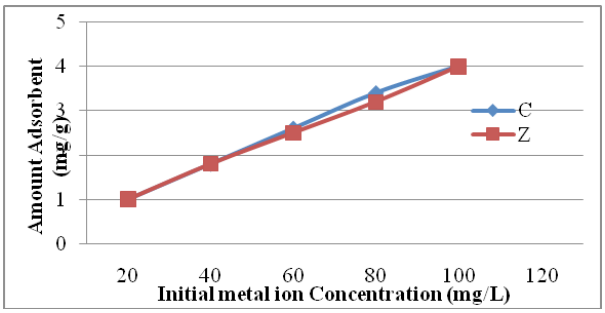


**Fig. 3.** Plot of sorption capacity vs initial concentration for adsorption of the Cu and Zn ions onto AH

### Adsorption Isotherms

The assessment of adsorption equilibrium typically involves employing an isotherm equation, which characterizes the surface properties and affinity of the adsorbent at constant temperature and pH (Ho, 2002). Adsorption equilibrium occurs when the content of a metal ion in the bulk solution (Ce) reaches a dynamic equilibrium with that at the interface. In the present study, the uptake capacities of metal ions were assessed using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models and the data are presented herein.

### The equilibrium Langmuir isotherm

The Langmuir isotherm describes the equilibrium partitioning of metal-ions between solid and liquid

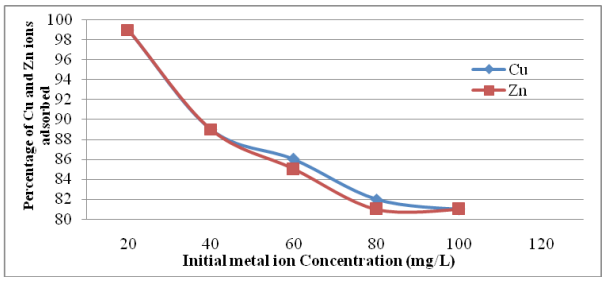


**Fig. 4.** Plot of percentage metal adsorbed vs initial conc. for adsorption of the metal-ions on AH

phases. It operates under several assumptions:

- Metal ions undergo chemical adsorption at a set number of distinct sites.
- Each site is capable of hosting only one ion, limiting coverage to a monolayer.
- All sites possess equivalent thermodynamic properties.
- There is no lateral interaction in the adsorbed metal-ions.

The linearized Langmuir isotherm equation enables the determination of the maximum adsorption capacity ($q_{max}$) associated with monolayer coverage, along with the Langmuir constant KL that signifies the strength of the adsorption process (Song, 2013 and Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad .. (5)$$

The equilibrium or residual concentration after adsorption (Ce) in mg/l, the equilibrium-adsorption-capacity ($q_e$) in mg/g, the maximum adsorption-capacity ($q_{max}$) in mg/g corresponding to monolayer coverage, and the Langmuir adsorption constant ($K_L$) are all parameters used to describe the adsorption process. The linear plots of $C_e/q_e$ versus Ce indicate that the adsorption process adheres to the Langmuir adsorption isotherm, as demonstrated in Figures 5.

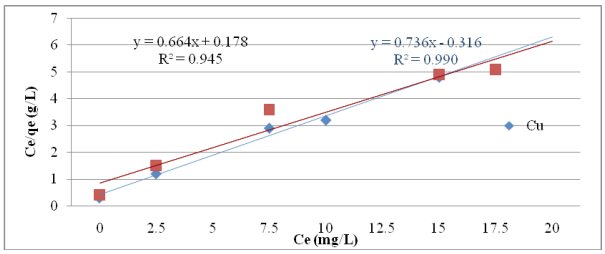


**Fig. 5.** Langmuir isotherm plot of Ce/qevsCe for adsorption of the metal-ions on the AH

Table 3 presents the Langmuir constants $K_L$ and $q_{max}$, alongside the $R^2$ values. The correlation coefficients ($R^2$ values) exceeding 0.90 for all metal ions indicate that the Langmuir Isotherm effectively interprets the adsorption data. The Langmuir constants, $q_{max}$, and $K_L$ were resultant from the linear plots' slope and intercept. Typically, $q_{max}$, representing the Langmuir capacity for monolayer coverage, is utilized to compare adsorbent efficiencies with other materials tested as biosorbents for metal ions in chemical literature. Table 3 summarizes the heavy metal adsorption

capacities (mg/g) of various common adsorbents, including bamboo dust and its activated form used in this study. Differences in adsorption capacities of adsorbent may stem from the types of functional groups on biosorbents, influencing their affinity for metal ions, as well as variations in particle size affecting surface area and porosity. In our study, bamboo dust adsorbed Cu and Zn at rates of 4.42 and 4.16 mg/l respectively, while bamboo-based activated charcoal adsorbed them at rates of 4.67 and 4.57 mg/l correspondingly, as shown in Table 3 alongside other adsorbents from literature. This indicates bamboo wastes effectiveness as adsorbents for removing these metal-ions from aqueous solutions. Additionally, our study reported that Cu was more proficiently adsorbed than Zn on adsorbent surfaces.

**Table 3.** Langmuir isotherm constants

| Constants | AH | |
|---|---|---|
| | Cu | Zn |
| $q_{max}$ (mg/g) | 4.8 | 5.1 |
| $K_L$ (mg/l) | 0.3 | 0.4 |
| $R_L$ | 0.032 | 0.042 |
| $R^2$ | 0.9458 | 0.9905 |

The Langmuir adsorption coefficient ($K_L$) for the metal ions exhibited high values, indicating a strong affinity of the adsorbent for these ions and suggesting a sharp onset of the isotherm for metal ion adsorption. The fundamental characteristics of Langmuir isotherms are further elucidated through a dimensionless parameter known as the separation factor (or equilibrium parameter), $R_L$ as given by equation no. 6.

$$R_L = \frac{1}{(1+K_L C_o)} \quad .. (6)$$

Here, $C_o$ represents the initial metal-ion concentration, and $K_L$ denotes the Langmuir constant. As described by McKay, 1987 and Horsfall *et al.*, (2004), the $R_L$ value indicates the shape of the isotherm: $R_L > 1$ signifies an unfavourable isotherm, $R_L = 1$ suggests a linear isotherm, $R_L = 0$ indicates an irreversible isotherm, and $0 < R_L < 1$ implies a favourable isotherm. The $R_L$ values attained for both metal-ions, Cu and Zn, on the two adsorbents at an initial concentration of 100 mg/l are all less than unity. This indicated that the isotherm was favourable under the conditions of our study and suggests that the adsorbents could serve as effective substrates for the removal of metal-ions.

**Equilibrium Freundlich Isotherm**

The Freundlich isotherm model was adopted to estimate the affinity of adsorbates, such as metal ions, for adsorbent. This model gives insight into the intensity of adsorption interactions. The linearized representation of the Freundlich adsorption isotherm is articulated as given in equation no. 7 (Anusiem, *et al.*, 2010):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad .. (7)$$

The parameters $K_F$ and $^1/_n$ in the Freundlich equation characterize the adsorption process in terms of its intensity and capacity, respectively. Figure 6 illustrates linear plots of ln $k_F$ versus ln $C_e$ adhering to the Freundlich isotherm equation. These plots allow for the determination of $K_F$ and from the intercept and slope, which are presented in figure 6. The $K_F$ values indicate the ease with which adsorption occurs, facilitating the separation of heavy metals from aqueous solutions. Meanwhile, the exponent, n, elucidates the distribution of bonded metal-ions on the adsorbent surfaces, thereby providing insight into the favourability and capacity of the adsorption process. Anusiem *et al.* (2010) noted that 'n' values falling between 1 and 10 signify favourable adsorption conditions. In this study, the exponent ranged from 2.382 to 2.798 across all cases, indicating advantageous adsorption for the system. The high $R^2$ values attained signify that the isotherm accurately interprets the adsorption behaviour of the metal ions (Freundlich, 1907).

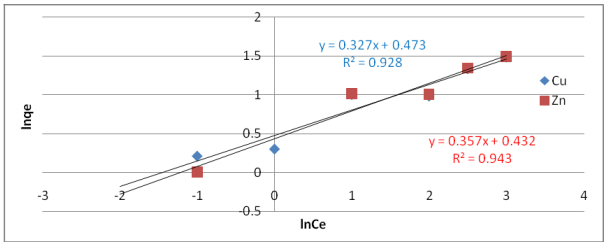


**Fig. 6.** Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal-ions onto AH

**Analysis of the Coefficient of Determination in Isotherm Models**

The coefficient of estimation ($R^2$) serves as a vital tool in regression analysis, elucidating the interplay between variables pivotal for assessing kinetic and thermodynamic parameters in adsorption processes. In the current study, various isotherm models such as Langmiur and Freundlich were employed to

scrutinize data. These models are represented by equations akin to y = mx + c (where m signifies slope and c represents intercept), underscoring the requisite linear relationship between y and x for predictive utility (Langmuir, 1918 and Freundlich, 1907).

$R^2$ signifies the extent to which variations in y values are explicable through the linear relationship with x, delineated by the regression line. A value of $R^2$ at zero suggests non-correlation between the variables, whereas a value of one indicates perfect correlation. Hence, $R^2$ values within the range of zero to one are instrumental in evaluating experimental data. The coefficients of determination for the isotherm models Langmuir and Freundlich were compared, with $R^2$ values approaching unity indicative of superior fitting models. In this investigation, the Freundlich isotherm emerged as the most apt descriptor for the adsorption phenomenon of the two metal ions, closely tracked by the Langmuir isotherm.

## CONCLUSION

This study has confirmed the efficacy of Arecanut Husk (AH) as adsorbent for removing Cu and Zn ions in aqueous solutions. The investigation focused on the encouragement of pH and metal ion concentration on the adsorption process. Results indicated a proportional increase in adsorption capacity with rising metal ion concentrations, with the more adsorption capacity of Cu and Zn occurring at pH 6.0. Analyzing the experimental data using Langmuir and Freundlich isotherm models revealed high $R^2$ values, with the Freundlich model exhibiting the best fit compared to Langmuir isotherm. AH exhibited superior affinity for Cu and Zn, and adsorbent demonstrated better removal capabilities for the metal ions compared to AH. The adsorption mechanism was identified as physisorption, supported by the outward energy of adsorption calculated from these models, In conclusion, AH show promise as effective adsorbent for eliminating Cu and Zn in aqueous solutions, suggesting potential applications in industrial wastewater treatment.

## ACKNOWLEDGEMENTS

The authors would like to express their appreciations to Srinivas University, Institute of Engineering and Technology, Mangaluru, Karnataka, India for providing place and complete this project.

**Conflict of Interest-** none

## REFERENCES

Abia, A.A. 2002. Studies on the Use of Agricultural Bi-Product for the Removal of Trace Metals from Aqueous Solution. *J. Appl. Sci. Environ. Mgt.* 6(2): 89-95.

Abia, A.A. 2003. The Use of Chemically-Modified and Unmodified Cassava Waste for the Removal of Cd, Cu and Zn Ions from Aqueous Solution.*Journal of Bioresource Technology*. 90(3) 345-348.

Amuda, O.S.A.O. 2006. Ibrahim.Industrial Wastewater Treatment for Chemical Oxygen Demand (COD) using Natural Material as Adsorbent. *African Journal of.Biotechnology*. 5(16): 1483-1487.

Anusiem, Aci, 2010. Adsorption Isotherm Studies of Ni (LI), Cd (LI) and Pb (LI) Ions from Aqueous Solutions by African White Star Apple (*Chrysophyllum albidiu*m) Shell. Intern.*Journ. Chem*. 20(4): 265-274.

Argun, M.E and Dursun, S. 2006. Removal of Heavy Metal Ions using Chemically Modified Adsorbents. *J. Int. Environ. Appl. Sci.* 1(1-2):27-40.

Argun, M.E. 2007. Heavy Metal Adsorptionby Modified Oak Sawdust: Thermodynamics and Kinetics. *Journal of Harzadous Materials*. 141: 77-85.

Asamudo, N.U. 2005. Bioremediation of Textile Effluent using Phanerochaete Chrysosporium. *African Journal of Biotechnology*. 4(13): 1548-1553.

Badmus, Mao, 2007. Removal of Lead Ion from Industrial Wastewaters by Activated Carbon Prepared from Periwinkle Shells. *Turkish J Eng Env Sc*. 31: 251-263.

Bansal, M. 2009. Use of Agricultural Waste for the Removal of Pb (LI) and Cd (LI) Ions from Aqueous Solutions: Equilibrium and Kinetic Studies. *Intern. Journ. Environ. Sci. Eng*. 1(2): 108-115.

Barka, Noureddine, 2013. Biosorption Characteristics of Cadmium and Lead onto Eco-Friendly Dried Cactus (*Opuntia ficusIndica*) Cladodes. *Journal of Environmental Chemical Engineering. Elsevier BV.* 1(3): 144-149. https://doi.org10.1016/j.jece.2013.04.008.

Dada, A.O. 2012. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of $Zn^{+2}$ Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry*. 3(1): 38-45.

Das, B. and N.K. 2011. Mondal. Calcareous Soil as a New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study. *Universal Journal of Environmental Research and Technology*. 1(4): 515-530.

Dawodu, Folasegun Anthony and Kovo Godfrey Akpomie, 2014. Simultaneous Adsorption of Ni(II) and Mn(II) Ions from Aqueous Solution unto a Nigerian Kaolinite Clay. *Journal of Materials Research and Technology.Elsevier BV.* 3(2): 129-141, https://doi.org10.1016/j.jmrt.2014.03.002.

Deepa, K.K. 2006. Sorption of Chromium (VI) from Dilute Solutions and Wastewaters by Live and Pretreated Biomass of Aspergillus Flavours. *Chemosphere.* 62(5):833-840.

Freundlich, H. 1907. Ueber die adsorption in Loesungen, Z. *Phys. Chem*. 57: 385-470.

Ho, Y.S. 2002. Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems. *Water, Air and Soil Pollution*. 141(1-4): 1-33.

Horsfall, M.J. 2004. Studies on the Influence of Mercaptoacetic Acid (MAA) Modification of Cassava (ManihotSculentaCranz) Waste Biomass on the Adsorption of $Cu^{2+}$ and $Cd^{2+}$ from Aqueous Solution. *Bulletin of the Korean Chemical Society*. 25(7): 969-976.

Hossain, M.A and Rahman, M.A. 2012. Equilibrium Adsorption of Rhodamine B on Used Black Tea Leaves from Acidic Aqueous Solution. *Orbital: The Electronic Journal of Chemistry*. 4: 187-201.

Hussein, Hany, 2004. Biosorption of Heavy Metals from Waste Wąter Using Pseudomonas Sp. *Electronic Journal of Biotechnology: EJB. Elsevier BV*. 7(1): 276-282, https://doi.org10.2225/vol7-issue1-fulltext-2.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc*. 40(9): 1361-1403.

Igwe, J.C. and Abia, A.A. 2007. Pb (II) and Zn (II) Ions Bioremediation from Aqueous Solution Using Unmodified and EDTA-Modified Maize Cob. *Eletica Quimica*. 32(1): 33-42.

Igwe, J.C. 2005. Cd(II) and Pb(II) Ions from Aqueous and Non-Aqueous Solution by Maize Cob and Husk. *African Journal of Biotechnology*. 4(10): 1113-1116.

Kehinde, O.O. 2009. Comparative Analysis of the Efficiencies of Two Low Cost Adsorbents in the Removal of Cr(VI) and Ni(II) from Aqueous Solutions. *African Journal of Environ. Sci. Technol.* 3(11): 360-369.

Khan, M.N and Wahab, M.F. 2006. Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution. *J. Hazard. Mater*. 141: 237-244.

Khani, M.H. 2006. Biosorption of Uranium from Aqueous Solutions by Nonliving Biomass of Marinealgae *Cystoseira indica. Electronic Journal of Biotech*. 9(2): 100-106.

Kumar, P. and Gayathri, R. 2009. Adsorption of $Pb^{2+}$ Ions from Aqueous Solutions onto Bale Tree Leaf Powder: Isotherms, Kinetics and Thermodynamics Study. *Journal of Engineering Science and Technology*. 4(4): 381-399.

Kumar, U. and Bandyopadhyay, M. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour.Technol.* 97: 104-109.

Kumar, U. 2006. Agriculture Products and By-Products as a Low-Cost Adsorbent for Sequesting Heavy Metal Ions from Aqueous Solutions: A Review. *Bioresource Technology*. 99(14): 65-90.

Yao, L., Ye, Z.F., Tong, M.P., Lai, P. and Ni, J.R. 2009. Ni. Removal of $Cr^{3+}$ from aqueous solution by biosorption with aerobic granules. *J. Hazard. Mater*. 165: 250-255.

McKay, Gordon, 1987. Mass Transport Processes for the Adsorption of Dyestuffs onto Chitin.Genie Des Procedes.*Chemical Engineering and Processing*. *Elsevier BV*. 21(1): 41-51, https://doi.org10.1016/0255-2701(87)80006-5.

Mishra, V. 2012. Kinetics, Mechanistic and Thermodynamics of Zn (II) Ion Sorption: A Modeling Approach. *Clean Soil Air Water*. 40(7): 718-727.

Mittal, Alok.Process Development for the Batch and Bulk Removal and Recovery of a Hazardous, Water-Soluble Azo Dye (Metanil Yellow) by Adsorption over Waste Materials (Bottom Ash and De-Oiled Soya). *Journal of Hazardous Materials*. 2008; 151(2-3): 821-832, https://doi.org10.1016/j.jhazmat.2007.06.059.

Muraleedharan, T.R. and Leela, I. Venkobachar, 1991. Biosorption: An Attractive Alternative for Metal Removal and Recovery. *Current Science*. 61: 379-385.

Nharingo, T. and Hunga, O. 2013. Equilibrium Isotherm Analysis of the Biosorption of $Zn^{2+}$ Ions by Acid Treated *Zea mays* Leaf Powder. *International Journal of Advances in Engineering and Technology*. 6(11): 28-139.

Oboh, I. 2009. Biosorption of Heavy Metal Ions from Aqueous Solutions Using a Biomaterial. *Leonardo Journal of Sciences*. 14: 11-17.

Okieimen, F.E. 1991. Sorption of Cadmium and Lead Ions on Modified Groundnut (Arachis Hypogea) Husks. *J. Chem. Technol. Biotectnol*. 51: 97-103.

Ong, S.A. 2007. Kinetics of Adsorption of Cu (LI) and Cd (LI) from Aqueous Solution on Rice Husk and Modified Rice Husk. *Electronic Journal of Environmental, Agriculture and Food Chemistry*. 6(2): 1764-1774.

Otitoju, O. and Gto Otitoju, 2013. Heavy Metal Concentrations in Water, Sediment and Periwinkle (*Tympanotonus fusca0stus*) Samples harvested from the Niger Delta Region of Nigeria. *African Journal of Environmental Science and Technology*. 7(5): 245-248.

Otitoju, O. 2012. Heavy Metal Contamination of Green Leafy Vegetable Gardens in Itam Road Construction Site in Uyo, Nigeria. Nigeria. *Research*

*Journal of Environmental and Earth Sciences*. 4(4): 371-375.

Qaiser, S. 2009. Biosorption of Lead (II) and Chromium (VI) on Groundnut Hull: Equilibrium, Kinetics and Thermodynamics Study. *Electronic Journal of Biotechnology*. 12(4)1-4.

Rangel, 2012. Vmm. As(V) Biosorption in an Aqueous Solution Using Chemically Treated Lemon (*Citrus aurantifoliaswingle*) Residues. *J Food Sci*. 77(1): 10-14.

Reed, Brian E. 1994. Removal of Lead and Cadmium from Aqueous Waste Streams Using Granular Activated Carbon (GAC) Columns. *Environmental Progress*. 13(1): 60-64. https://doi.org10.1002/ep.670130119.

Sajidu, Smi, 2006. pH Dependence of Sorption of $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ on Crude Water and Sodium Chloride Extracts of MoringaStenopetala and MoringaOleifera. *African Journal of Biotechnology*. 5(23): 2397-2401.

Sastre de Vicente and Manuel Esteban, 2004. Biosorption of Cadmium by FucusSpiralis.*Environmental Chemistry (Collingwood, Vic.)*. 1(3): *CSIRO Publishing*, 180. https://doi.org10.1071/en04039.

Sharma, Shikha and Deepak Pathania and Pardeep Singh, 2013. Preparation, Characterization and Cr(VI) Adsorption Behavior Study of Poly(Acrylic Acid) Grafted FicusCaricaBastFiber. *Advanced Materials Letters*.*International Association of Advanced Materials*. 4(4): 271-276, https://doi.org10.5185/amlett.2012.8409.

Shukla, S.R. and Pai, R.S. 2005a. Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. *Bioresour. Technol*. 96: 1430-1438.

Shukla, S.R and Pai, R.S. Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. Sep. *Purif. Technol*. 2005b; 43: 1-8

Song, Chengwen, 2013. Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation for Removal of Lead(II) from Aqueous Solutions. *Sustainability*. 6(1): 86-98. https://doi.org10.3390/su6010086.

Sud, Dhiraj, 2008. Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions - a Review.*Bioresource Technology*. *Elsevier BV*. 99(14): 6017-6027, https://doi.org10.1016/j.biortech.2007.11.064.

Tchuifon, D.R. 2014. Equilibrium and Kinetic Modeling of Methyl Orange Adsorption from Aqueous Solution Using Rice Husk and Egussi Peeling.*Intern.Journ. Chem. Sci.* 12(3):741-761.

Ucer, 2006. Mn(II) and Fe(III) Ions by Tannic Acid Immobilised Activated Carbon, Sep. Adsorption of Cu(II), Cd(II), Zn(II). *Separation and Purification Technology*. 47: 113-118.

Vargas, K.K. 2012. Biosorption of Heavy Metals in Polluted Water, Using Different Waste Fruit Cortex. *Physics and Chemistry of the Earth*. 39: 26-29.

Vasudevan, Padma, 2002. Biosorption of Monovalent and Divalent Ions on Baker's Yeast.*Bioresource Technology*. *Elsevier BV*. 82(3): 285-289. https://doi.org10.1016/s0960-8524(01)00181-x.

Veglio F. and Beolchini, F. 1997. Removal of metals by biosorption: A review. *Hydrometallurgy*. 44: 301-316.

Viraraghavan, T. and Dronamraju, M.M. 1993. Removal of Copper, Nickel and Zinc from Wastewater by Adsorption Using Peat.*J. Environ. Sci. Health Part A. Environ. Sci. Eng*. 28: 1261-1276.

Volesky, B. 1994. Advances in Biosorption of Metals: Selection of Biomass Types FEMS. *FEMS. Microbiol*. 14: 291-302.

Wang, X.S., Tang, Y.P and Tao, S.R. 2009. Kinetics, equilibrium and thermodynamic study on removal of Cu(II) using low-cost adsorbent alligator weed. *Chem. Eng. J*. 148: 217-225.

Weber, Walter J. 1991. Sorption Phenomena in Subsurface Systems: Concepts, Models and Effects on Contaminant Fate and Transport. *Water Research. Elsevier BV*. 25(5): 499-528, https://doi.org10.1016/0043-1354(91)90125-a.

Yang, Ru, 2011. Surface Texture, Chemistry and Adsorption Properties of Acid Blue of Hemp (*Cannabis sativa* L.) Bast-Based Activated Carbon Fibers Prepared by Phosphoric Acid Activation. *Biomass & Bioenergy*. *Elsevier BV*. 35(1): 437-445, https://doi.org10.1016/j.biombioe.2010.08.061.