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## **DEVELOPMENT OF NATURAL ADSORBENT COLLECTED FROM ABECHÉ: CHARACTERIZATION AND UTILIZATION IN THE REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER DISCHARGED IN THE CITY OF N'DJAMENA (CHAD)**

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### **ABSTRACT**

Industrial wastewater discharged in the city of N'Djamena (Chad) contains substantial concentrations of heavy metals and alkalinity-related ions that threaten aquatic ecosystems and public health. This study evaluates the efficiency of a low-cost biosorbent prepared from peanut (groundnut) husks for the simultaneous removal of five heavy metals ions (remove metal ions such as  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Cr^{3+}$ ) and three alkalinity-related base cations (calcium, potassium and sodium) from three real industrial wastewater samples collected in N'Djamena. Batch adsorption experiments were carried out using acid/base-washed peanut husk powder of controlled particle size (200–300  $\mu m$ ), and metal concentrations were determined by atomic absorption spectrophotometry (ISO 8288) before and after treatment. Removal efficiency (RE, %) was calculated for each element, and a Tobit regression model was applied to properly account for left-censored (below-detection-limit) measurements, while a linear mixed-effects model assessed the combined effects of treatment and metal type on concentration, with

sample included as a random effect. Chromium showed the highest removal efficiency among the heavy metals (80.8%), followed by cadmium (68.9%) and lead (55.0%), whereas zinc and copper displayed strongly negative removal efficiencies (−513.3 % and −158.3%, respectively), indicating a net release of these elements from the adsorbent matrix. Among the alkalinity metals, sodium was efficiently removed (81.5%), while calcium and potassium concentrations increased after treatment (−215.3 % and −38.9%, respectively). Tobit regression confirmed that the initial concentration was the only statistically significant predictor of residual concentration ( $\beta = 0.2588$ ,  $p < 0.001$ ), regardless of metal type ( $p > 0.05$ ). These findings demonstrate that peanut husk behaves as a selective, low-cost biosorbent, particularly effective for chromium, cadmium, lead and sodium, but that further optimization of dose, pH and contact time is required to limit the release of zinc, copper, calcium and potassium into treated water.

**Keywords:** Heavy metals, Adsorption, Bio sorption, Peanut shells, Agricultural waste

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## 1. INTRODUCTION

The uncontrolled discharge of industrial wastewater—from breweries, slaughterhouses, cement plants, tanneries, textile and electroplating industries, among others—is a major and growing source of environmental contamination. Unlike organic pollutants, heavy metals such as chromium, cadmium, lead, zinc and copper are non-biodegradable and tend to bioaccumulate in living organisms, causing serious health problems in animals, plants and humans, including cancer, kidney failure, metabolic acidosis and other chronic disorders [El-Sharkawy et al. (2001) (1); Jern (2006) (2); Ayyappan et al. (2005) (3); Lee et al. (2012) (4); Stasinakis and Thomadis (2010) (5)].

Conventional treatment technologies—chemical precipitation, ion exchange, membrane filtration and electrochemical processes—are effective but remain costly and may generate secondary pollution, particularly for small and medium-scale industries in low-resource settings [Elkady et al. (2016) (6); Al-Ashesh et al. (2000) (7)]. This has motivated growing interest in low-cost, environmentally friendly alternatives based on agricultural residues. Lignocellulosic wastes such as rice husks, sawdust, orange peels and peanut husks contain surface functional groups (hydroxyl, carboxyl and phenolic moieties) capable of binding metal ions through adsorption and ion exchange, making them attractive substitutes for costlier conventional adsorbents [Shih (2012) (8); Naushad et al. (2016) (9); Dhir (2014) (10)].

Among agricultural residues, peanut shells have received particular attention owing to their abundance, low cost, high porosity and favorable surface chemistry. Previous studies using raw, chemically modified, or activated peanut shells have reported effective removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Cr^{3+}$ , as well as dyes and other contaminants, mostly from synthetic single-metal solutions under controlled laboratory conditions [Wafwoyo et al. (1999) (11); Brown et al. (2000) (12); Wang et al. (2015) (13); Ricordel et al. (2001) (14); Chamarthy et al. (2001) (15); Ouyang et al. (2014) (16); Li et al. (2007) (17); Al-Othman et al. (2012) (18)]. However, fewer studies have evaluated peanut husk-based biosorbents on real, multi-element industrial effluents, or have applied statistically rigorous methods capable of handling

concentrations reported below the analytical detection limit—a common occurrence in environmental monitoring data that, if ignored or naively substituted, can bias removal-efficiency estimates.

The objective of the present study is therefore to evaluate the efficiency of a peanut husk-derived adsorbent for the simultaneous removal of five heavy metals (Cr, Cd, Pb, Zn, Cu) and three alkalinity-related base cations (Ca, K, Na) from real industrial wastewater samples collected in N'Djamena, Chad, and to characterize this removal quantitatively using removal-efficiency calculations together with Tobit regression and linear mixed-effects modeling to properly account for left-censored data and sample-to-sample variability.

## **2. MATERIALS AND METHODS**

### **2.1 Samples collection**

The samples of industrial wastewater used in this research were collected from the industrial districts of the city of N'Djamena (Chad) using standard methods.

### **2.2 Determination of heavy metals and alkalis metals**

The heavy metals, alkalis metals in industrial wastewater are determined by using Atomic Absorption spectrophotometer (SAFAS AA170) and ISO 8288.

### **2.3 Adsorbent for removing heavy metals and alkalis metals**

The Characterization of agricultural adsorbents: Low cost, environmentally friendly, Possibility of physical and chemical modification, good adsorption capacity for heavy metals in wastewater and best alternatives for removing heavy metals from industrial effluents.

### **2.4 The optimal conditions for agricultural adsorbents**

Adsorbent dose, contact time, PH adjustment, Adsorbent particle size and temperature, Agricultural waste (peanut husks) has been used as a natural adsorbent for removing heavy metals from industrial wastewater.

### **2.5 Chemical and reagents**

All solutions:  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  at 100mg/l,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at 100mg/l,  $(\text{Pb}(\text{NO}_3)_2)$  at 100mg/l,  $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$  at 100mg/l  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{Ca}_3\text{CO}_2)$ , at 100mg/l  $(\text{CdSO}_4 \cdot 8\text{H}_2\text{O})$ , at 100mg/l  $(\text{NaCl})$  at 100mg/l  $(\text{KCl})$  at 100mg/l prepared from analytical grade chemicals and distilled water. Diluted HCl acid, diluted NaOH base and buffer solutions for pH calibration are used.

## **3. PREPARATION OF THE ADSORBENT MATERIAL FROM PEANUT HUSKS**

The peanut husks were collected from my farm on the outskirts of Abéché (Ouaddaï) and washed several times with tap water (cold) to remove dirt and other impurities. In addition, the soluble and coloring components of the shells were removed by washing them repeatedly with hot water (80°C) until the water became colorless, then distilled water. The washed peanut shells were dried at room temperature, and then dried in a thermal oven at 80°C for 12 hours to remove moisture. It was ground in a mill to form a shell powder, then sieved several times. The peanut shell powder was separated into particles measuring 200 to 300 micrometers. Then the adsorbent was soaked in distilled water to remove any organic matter stuck to it and dissolve it completely. The mixture was filtered, and the adsorbent, consisting of bean powder, was soaked in diluted sodium hydroxide and diluted hydrochloric acid, respectively. The adsorbent was

washed several times with distilled water to remove any traces of acidity. This filtered biomass was dried at room temperature, then in an oven at 80°C Celsius for 12 hours. The dried absorbent material was stored in tightly sealed glass containers to protect it from moisture. After preparing the adsorbent and absorbent material (heavy metal wastewater samples) in **100ml** volumetric flasks, the samples were divided into two halves in the first the **pH** was adjusted to 4 and that of the second the **pH** at 6.5-7. Next, the adsorbent was weighed and placed directly into **100 ml** volumetric flasks, where **3 g** of adsorbent was placed in the first and **4 g** in the second flask. All volumetric flasks were then placed in an electronic shaker for six hours intermittently to complete the process of transferring the material to the adsorbent. The mixture was then filtered through Whatman paper in order to reanalyze the sample and compare the concentrations of heavy elements before and after treatment with the adsorbent [Barkin D, et al. (2000) (19)]. The results were as follows:

**Table 1: Concentrations of Heavy Metals Before and After Treatment with Peanut husk Adsorbent**

| Sample | Element  | Before_treat | After_treat | LOD   | Censored | PH_before | PH_after |
|--------|----------|--------------|-------------|-------|----------|-----------|----------|
| 1      | Zinc     | 0.02         | 0.071       | 0     | False    | 6.5       | 4        |
| 1      | Chromium | 0.08         | <0.01       | 0.01  | True     | 6.5       | 4        |
| 1      | Lead     | <0.01        | 0.01        | 0     | False    | 6.5       | 4        |
| 1      | Cadmium  | 0.01         | <0.002      | 0.002 | True     | 6.5       | 4        |
| 1      | Cooper   | 0.01         | 0.04        | 0     | False    | 6.5       | 4        |
| 2      | Zinc     | 0.01         | 0.101       | 0     | False    | 6.5       | 4        |
| 2      | Chromium | 0.2          | 0.05        | 0     | False    | 6.5       | 4        |
| 2      | Lead     | 0.01         | 0.002       | 0     | False    | 6.5       | 4        |
| 2      | Cadmium  | 0.003        | <0.002      | 0.002 | True     | 6.5       | 4        |
| 2      | Cooper   | 0.04         | 0.05        | 0     | False    | 6.5       | 4        |
| 3      | Zinc     | 0.02         | 0.095       | 0     | False    | 6.5       | 4        |
| 3      | Chromium | 0.3          | 0.06        | 0     | False    | 6.5       | 4        |
| 3      | Lead     | 0.02         | 0.003       | 0     | False    | 6.5       | 4        |
| 3      | Cadmium  | 0.03         | <0.002      | 0.002 | True     | 6.5       | 4        |
| 3      | Cooper   | 0.02         | 0.05        | 0     | False    | 6.5       | 4        |

**Table 2: Concentrations of Alkalinity Metals Before and After Treatment with Peanut husk Adsorbent**

| Sample | Element   | Before_trea | PH_Before | After_treat | PH_After |
|--------|-----------|-------------|-----------|-------------|----------|
| 1      | Calcium   | 0.004       | 6.5       | 0.0085      | 4        |
| 1      | Potassium | 0.168       | 6.5       | 0.221       | 4        |
| 1      | Sodium    | 0.176       | 6.5       | 0.0323      | 4        |
| 2      | Calcium   | 0.009       | 6.5       | 0.03        | 4        |
| 2      | Potassium | 0.272       | 6.5       | 0.446       | 4        |
| 2      | Sodium    | 0.178       | 6.5       | 0.0326      | 4        |
| 3      | Calcium   | 0.010       | 6.5       | 0.04        | 4        |
| 3      | Potassium | 0.306       | 6.5       | 0.371       | 4        |
| 3      | Sodium    | 0.175       | 6.5       | 0.0327      | 4        |

### 3.1. Statistical analysis

Statistical analyses were performed using the R statistical software. Descriptive analyses were initially conducted to evaluate variations in metal concentrations before and after treatment with peanut husk adsorbent. Graphical representations, including concentration comparison plots and removal efficiency diagrams, were used to visualize treatment performance.

Because some concentrations were reported below the analytical detection limit (LOD), left-censored observations were considered in the statistical analysis. A Tobit regression model was applied to account for censored measurements and to avoid potential bias associated with conventional substitution methods such as replacing values below the LOD by LOD/2. The Tobit model was expressed as:

$$Y_i^* = \beta_0 + \beta_1 X_1 + \dots + \beta_p X_{pi} + \varepsilon_i$$

where  $Y_i^*$  represents the latent post-treatment concentration,  $X_i$  includes explanatory variables such as initial concentration and metal type, and  $\varepsilon_i$  is the error term.

Removal efficiency (RE) was calculated according to:

$$RE(\%) = \frac{C_{before} - C_{after}}{C_{before}} \times 100$$

Where  $C_{before}$  and  $C_{after}$  are the metal concentrations before and after treatment, respectively.

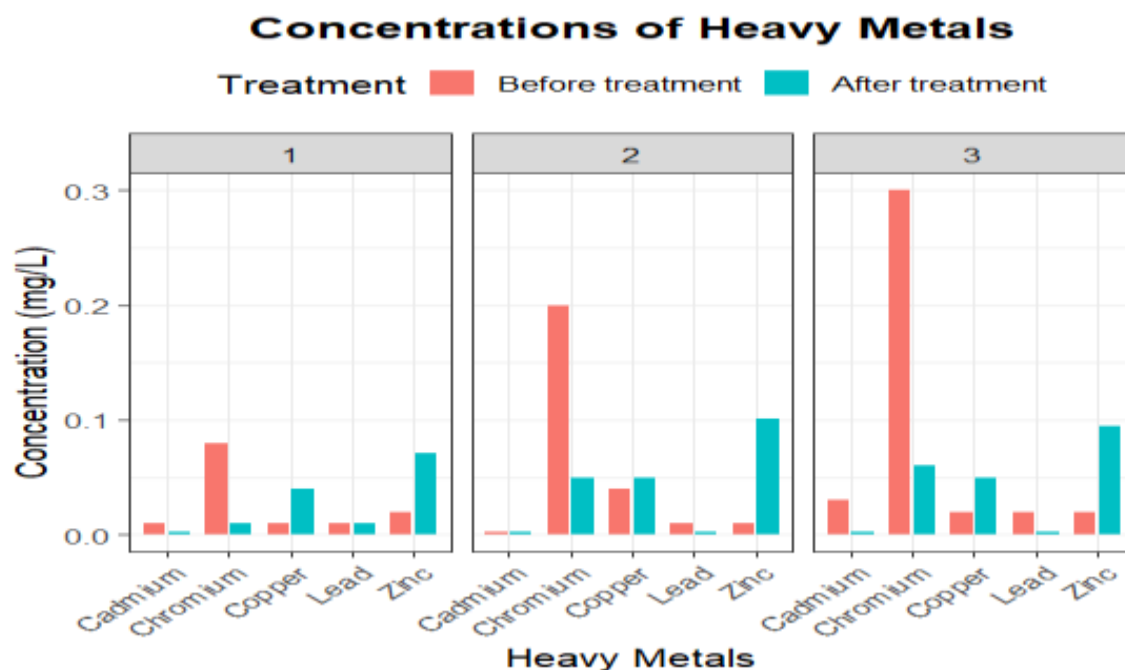
For alkalinity metals, a linear mixed-effects model was also considered:

$$\text{Concentration} \sim \text{Treatment} \times \text{Element} + (1 \mid \text{Sample})$$

Where treatment (before/after) and metal type were considered fixed effects, while sample variability was included as a random effect. Statistical significance was evaluated at a 5% significance level ( $p < 0.05$ ).

## 4. RESULTS AND DISCUSSION

### 4.1. Effect of peanut husk treatment on heavy metal concentrations



**Figure 1: Concentrations of heavy metals**

Figure 1 presents the concentrations of heavy metals before and after treatment using peanut husk adsorbent for three independent wastewater samples. The results indicate a metal-dependent adsorption behavior, suggesting that the efficiency of peanut husk strongly depends on the physicochemical properties of each element.

Chromium (Cr) exhibited the most consistent reduction after treatment. The concentrations decreased from 0.08 to 0.01 mg L<sup>-1</sup>, from 0.20 to 0.05 mg L<sup>-1</sup>, and from 0.30 to 0.06 mg L<sup>-1</sup> for Samples 1, 2, and 3, respectively. This significant decrease highlights the strong affinity between chromium species and the functional groups present on the lignocellulosic surface of peanut husk, including hydroxyl, carboxyl, and phenolic groups.

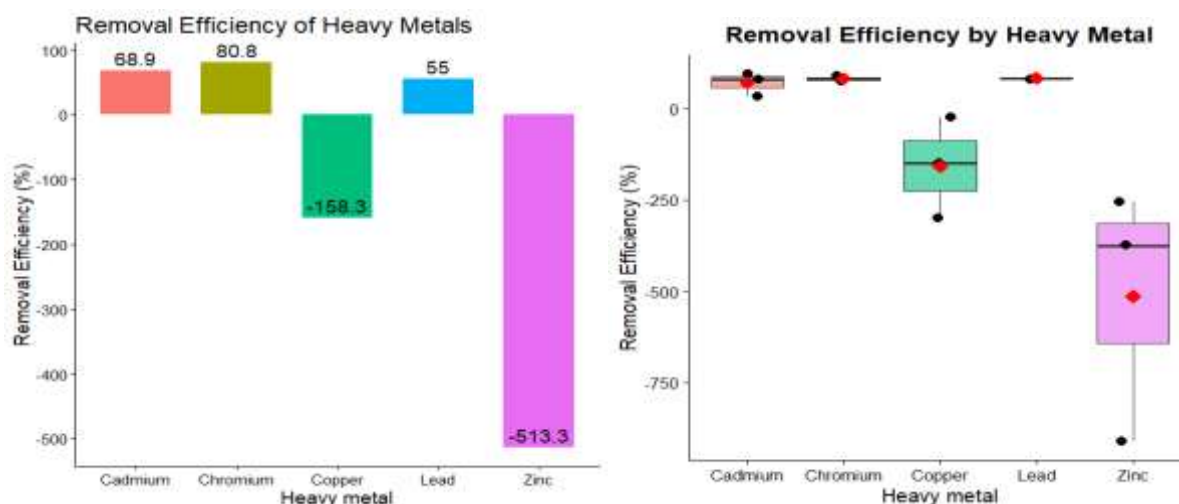
In contrast, zinc (Zn) concentrations increased after treatment, changing from approximately 0.02 to 0.07 mg L<sup>-1</sup>, 0.01 to 0.10 mg L<sup>-1</sup>, and 0.02 to 0.095 mg L<sup>-1</sup> for the three samples. Copper (Cu) showed a similar trend, indicating limited adsorption efficiency under the experimental conditions. These increases may be explained by competitive adsorption mechanisms, desorption phenomena, or the release of trace amounts of Zn and Cu initially present in the peanut husk matrix.

Cadmium (Cd) and lead (Pb) concentrations remained relatively low throughout the experiment. Although slight decreases were observed after treatment, the magnitude of change was limited due to their initially low concentrations.

Overall, these results demonstrate that peanut husk exhibits selective adsorption behavior. Chromium was

the most effectively removed element, whereas zinc and copper showed poor removal performance. Such differences may be related to variations in ionic radius, hydration energy, charge density, metal speciation, and competition for adsorption sites.

#### 4.2. Removal efficiency of heavy metals



**Figure 2: Removal Efficiency of heavy metals**

The removal efficiency values obtained for heavy metals are presented in Figure 2. The adsorption performance varied considerably among elements, confirming the selective nature of peanut husk toward different metal ions.

Chromium showed the highest removal efficiency (80.8%), followed by cadmium (68.9%) and lead (55.0%). These positive removal efficiencies confirm the ability of peanut husk to reduce these contaminants effectively.

The high chromium removal efficiency may be attributed to the strong interaction between chromium ions and active functional groups on the biosorbent surface. Similarly, the removal of cadmium and lead suggests favorable adsorption interactions between these metals and the peanut husk structure. Conversely, zinc and copper exhibited negative removal efficiencies, reaching  $-513.3\%$  and  $-158.3\%$ , respectively. Negative removal efficiency indicates that concentrations after treatment were higher than initial concentrations. This behavior suggests possible release of these elements from the adsorbent, insufficient adsorption capacity, or competitive interactions among metal ions. Therefore, peanut husk appears to be a promising low-cost biosorbent mainly for chromium, cadmium, and lead removal, whereas additional optimization is required to improve its efficiency toward zinc and copper.

#### 4.3. Tobit regression analysis

The Tobit regression model was applied to evaluate the factors influencing post-treatment concentrations

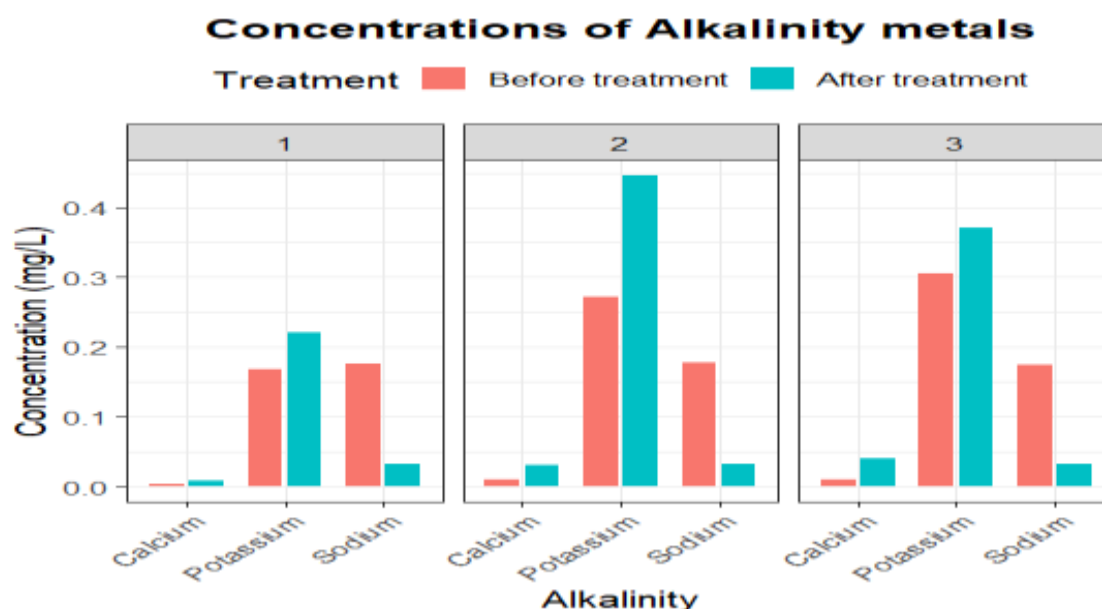
while accounting for left-censored observations.

The results showed that initial concentration was the only significant predictor of residual concentration after treatment:

$$\beta = 0.2588, p < 0.001$$

indicating that samples with higher initial contamination levels tended to exhibit higher residual concentrations after treatment. However, the effect of metal type was not statistically significant ( $p > 0.05$ ). These results suggest that, after accounting for censoring, the variation in post-treatment concentrations was mainly explained by initial contamination levels rather than by metal category alone. The use of the Tobit approach provides a more reliable estimation compared with simple substitution methods because it incorporates the uncertainty associated with concentrations below the detection limit.

#### 4.4. Effect of peanut husk treatment on alkalinity metals

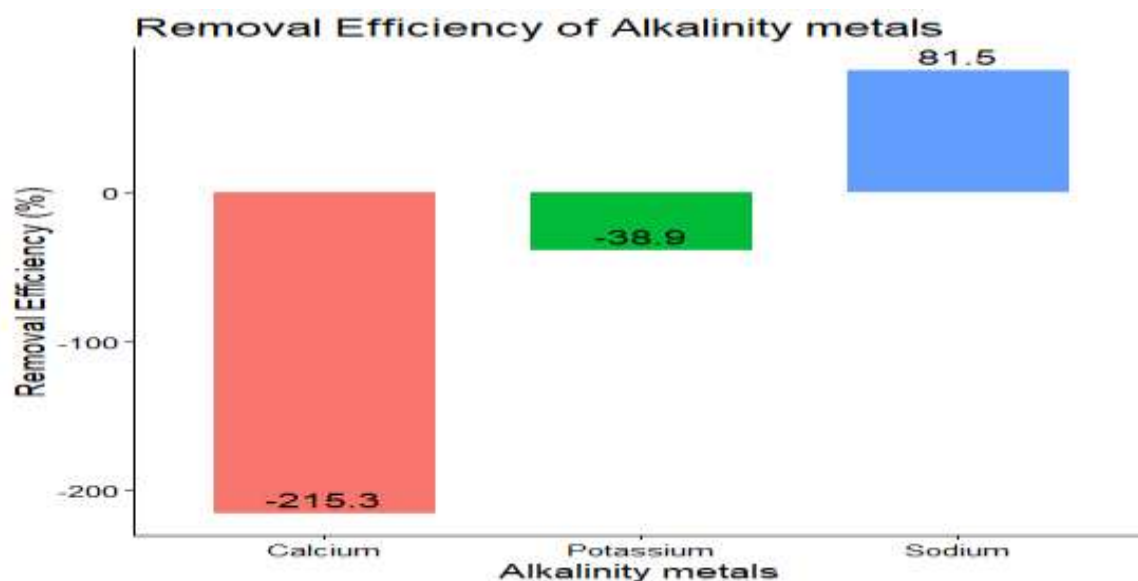


**Figure 3: Concentrations of Alkalinity metals before and After Treatment**

Figure 3 illustrates the concentrations of calcium (Ca), potassium (K), and sodium (Na) before and after treatment. The treatment produced different effects depending on the element. Sodium concentration decreased substantially after adsorption, from approximately  $0.18 \text{ mg L}^{-1}$  before treatment to values below  $0.04 \text{ mg L}^{-1}$  after treatment.

In contrast, calcium concentration increased slightly after treatment, whereas potassium showed a moderate increase, with concentrations increasing from approximately  $0.17\text{--}0.31 \text{ mg L}^{-1}$  to  $0.22\text{--}0.45 \text{ mg L}^{-1}$ . The removal efficiency analysis (see figure 4 below) confirmed these contrasting behaviors. Sodium

exhibited high positive removal efficiency (81.5%), indicating effective removal by peanut husk. Conversely, calcium and potassium showed negative removal efficiencies of -215.3% and -38.9%, respectively, suggesting a release of these ions from the adsorbent material.



**Figure 4: removal efficiency of Alkalinity metals**

These results indicate that peanut husk does not act only as an adsorbent but may also participate in ion exchange processes, releasing certain mineral components into the treated water.

#### 4.5. Mixed-effects model analysis

A linear mixed-effects model was fitted to evaluate the effects of treatment (before vs. after adsorption), metal type, and their interaction on heavy metal concentrations while accounting for variability among samples. Treatment and metal type were considered fixed effects, whereas sample was included as a random effect. In addition, removal efficiency (RE) was calculated for each metal and analyzed using a linear model. The results showed that sodium exhibited the highest removal efficiency (approximately 81%), whereas calcium and potassium displayed negative removal efficiencies, indicating an increase in concentration after treatment. These findings suggest that peanut husk adsorbent is effective for sodium removal but ineffective for calcium and potassium under the experimental conditions.

### 5. CONCLUSION

The statistical analysis demonstrated that peanut husk adsorption efficiency strongly depends on the chemical nature of the element. Chromium showed the highest removal performance among heavy metals, while zinc and copper were poorly removed and may have been released from the adsorbent matrix. Sodium was effectively removed among alkalinity metals, whereas calcium and potassium concentrations increased after treatment. The Tobit model provided a robust framework for analyzing censored

concentration data and confirmed that initial concentration was the main determinant of residual contamination. Overall, peanut husk represents a promising low-cost biosorbent, particularly for chromium and sodium removal, although further optimization is required to enhance its selectivity toward other elements.

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