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# Assessment of the Potentials of *Theobroma Cacao* Pod-Feldspar Composite Adsorbent for Heavy Metal Removal in Waste Water

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## Abstract

**Purpose:** Most conventional wastewater treatment techniques for the removal heavy metals are highly expensive and may, create sludge disposal problems. Adsorption techniques are relatively cheaper particularly when the process is carried out using low-cost materials and biomass. This paper is on the assessment of the potentials of a modified feldspar composite absorbent developed from waste agricultural biomass (*Theobroma cocoa* pod) and feldspar mineral in the removal of heavy metals from wastewater.

**Methodology:** The physicochemical analysis were carried out on the wastewater samples before and after treatment with modified feldspar composite using standard methods. Portions of the samples were directly digested and analysed for Pb, Cd, Cr and As, while the second portions were treated with the modified *Theobroma cocoa* pod-Felspar (TCPF) adsorbent under optimum conditions before analysing for the heavy metals. The desorption (cleaning) of the TCPF adsorbent after the adsorption of the heavy metals (Pb, Cd, As and Cr) from the wastewater was carried out with 0.1 M HCl.

**Findings:** The AAS analysis revealed that, the concentrations of the heavy metals in the wastewater before treatment with TCPF were higher and followed Pb>Cr>Cd>As trend and were above WHO and NESREA standards. The values for the samples treated with TCPF were lower and followed Cr>As>Pb>Cd trend and were within the standards. The differences between the values for the individual metals in the wastewater before and after treatment with the TCPF adsorbent were significant at $p< 0.05$. The adsorption efficiency of the TCPF was high for Pb (98.92%), Cd (96.88%) and Cr (97.18). Similarly, the TCPF showed high desorption efficiency with 76.8% for Pb, 90.6% for Cd, 94.4% for As and 80.3% for Cr.

**Unique contribution to theory policy and practice:** The modified composite (TCPF) has shown some significant potentials for use in the removal of the selected heavy metals from wastewater and industrial effluent.

**Key words:** *Theobroma cocoa pod Modified feldspar composite, Wastewater, Heavy metals*

## 1. Introduction

The pollution of water bodies by industrial effluents is a serious environmental challenge in recent times due to the increased industrial activities (such as batteries recycling, mining, pharmaceuticals, metallurgy, tannery and paints [1, 2]. The heavy metals present in water bodies above the acceptable limit are severe hazards to humans and ecosystems [3, 4]. Heavy metals are one of the most worrisome pollutants in the environment due to their potential toxicity, persistence and bio-accumulation problems. Direct toxicity to man and other forms of life and indirect toxicity through the food chains are the focus of this concern [5].

To maintain a healthy living, some metals with high nutritional value such as Copper, Iron, Zinc and Manganese are required either as a micro-nutrient or macro-nutrients. However, some others like Cadmium, lead and Arsenc are poisonous, increased exposure to these metals can be extremely hazardous as they damage nerves, brain, liver, heart, lung and bones as well as inhibit enzyme activity [6]. In order to combat threat to the environment and thus human health, it is highly essential to reduce the concentration of these metal ions to a tolerable limit in municipal and industrial effluents prior to final release into the natural water sources [3, 4, 7, 8].

To alleviate the problem of water pollution by heavy metals, various conventional methods including precipitation, coagulation, floatation, adsorption, ion exchange, reverse osmosis, ultrafiltration, electro-dialysis and membrane processes have been used. However, most of these methods of treatment suffer several techno-economic limitations such as inefficiency, cost expensive, sludge production, membrane instability [4]. Removal of toxic chemical substances by adsorption using natural materials is the latest method of choice in the water treatment process. This is due to the several techno-economic advantages associated with natural materials when compared with others in water treatment process; cheapness, easy to obtain and processed, availability, efficient in terms of adsorption and environmentally friendly [9, 10].

Among the most promising natural materials used as alternative adsorbents are aluminosilicate minerals (i.e feldspar) and agricultural wastes. The utilization of feldspar and its derivatives and agro-wastes would solve the disposal problem, and also provide access to less-expensive materials for wastewater treatment. Due to their low production costs, clays and agro-wastes could be easily regenerated after use which provide more advantages in using them as adsorbents [11]. In spite of the very attractive adsorption properties of feldspar, clays and agro-wastes, it is still very cumbersome to utilize these adsorbents on industrial scales for reasons like clogging, difficulty in recovery from industrial sieves, very low flow rates (≈2 mL/min) for clays infixed bed columns, inefficiency in removal of very low heavy metal concentrations from aqueous solutions, low density, “bleeding”, and/or decomposition of the biosorbents when left in aqueous solution for some longer period of time. These drawbacks have limited their potentials for adsorption applications [7, 8, 12].

In order to circumvent these limitations, modification methods such as intercalation, pillaring, organic surface treatment, thermal activation, acid-alkaline treatment and others have been used [13]. Recently, modification method involving synergistic combination of aluminosilicate materials and agricultural wastes (both being low cost adsorbents) are beginning to receive attention for subsequent improvement on adsorption capacity of the new adsorbents produced. *Theobroma cacao* pod-feldspar composite (TCPF) exploits the advantage of the adsorption characteristics of each adsorbent that yield the new composite. Such synergistic combinations often lead to better adsorbent properties such as high cation exchange capacity (CEC), eliminate bleeding, good adsorption efficiency, durability, re-usability, larger surface area and even comparatively lower cost for water treatment [8].

Both the feldspar sample used for this studies and the *Theobroma cacao* pod-feldspar composite were earlier characterized and used in the adsorption of heavy metals in aqueous solution. The feldspar was found to be a typical of K-feldspar and the crystal structure of the feldspar (XRD Analysis) was not affected by the modification process. The *Theobroma cacao* pod-modified feldspar composite showed an improved ion-exchange capacity and the FTIR analysis on the TCPF after calcination indicated a successful synthesis of the modified composite. The SEM analysis of the TCPF modified composite showed some level of increase in the surface area. Similarly, in the batch adsorption experiment conducted on the TCPF, the values of 1.0g, 2-6, 120 min, and 300 K were reported as the optimum for the adsorbent dose, pH, contact time and temperature respectively in the adsorption of Lead, Cadmium, Arsenic and Chromium. The desorption test conducted on the TCPF revealed that using 0.1MHCl as cleaning agent was able to clean it for another use [7, 8, 14]. Therefore, an absorbent derived from *Theobroma cacao* (cocoa) pod and feldspar (i.e. a modified composite) would remove heavy metals efficiently from wastewater containing heavy metals. This study therefore investigate the effectiveness of the *Theobroma cacao* pod-modified feldspar composite in adsorption of heavy metals (Cd, Pb, As, and Cr) in wastewater samples.

## 2.0 Material and Methods

### 2.1 Materials

**Sample Collection and preparation**

*Theobroma cacao* pods (TCP) were collected from cocoa plantations in Ifetedo town, Osun State. The TCP samples were washed with tap water and then rinsed with distilled water to remove dust, dirt impurities, oven-dried at 70$^\circ$C for 72 h and ground to powder using mortar and pestle. The TCP was sieved in a 0.230 mm sieve and stored in plastic container [7, 13, 15]. The feldspar (FS) sample was obtained from the Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria. The feldspar sample was pre-treated by suspension in deionized water for 24 h [7, 8, 14]. The organic matters in the sample were removed by adding 30% hydrogen peroxide solution with stirring until effervescence ceased. The mixture was decanted, washed with deionized water to remove all traces of hydrogen peroxide, oven-dried at 105˚C and stored in a pre-cleaned dry air-tight plastic container [8, 9, 14]

## 2.2 Methods

### 2.2.1 Preparation of *Theobroma cacao* pod-Feldspar Adsorbent (TCPF)

Equal weight of feldspar and TCP samples (50 g each) were weighed into a 500 mL beaker and 300 mL of 0.1M NaOH was added. The content was thoroughly stirred and heated in an oven at 105˚C until dryness [8, 9]. Samples of the dried mixtures were weighed into crucibles and calcined at 300˚C for 6 h. The resulting dark powdery composite was washed with deionized water to remove residual NaOH from its surface. The *Theobroma cacao* pod-feldspar composite adsorbent (TCPF) was oven-dried at 105˚C and stored in a dry plastic container [7, 12, 14].

### 2.2.2 Wastewater Sample Collection and Preservation

About 2 litres of wastewater from GERAN lead-acid battery recycling centre were collected on 27$^{th}$, 28$^{th}$ and 29$^{th}$ of November,2022 in the early morning hours at the point of discharge into Ogunpa River using 2 litre pre-cleaned plastic bottles. The samples were labelled as A, B and C respectively. The samples were transported to the laboratory and stored at about 4$^{\circ}$C in a refrigerator prior to analysis [16, 17].

### 2.2.3 Wastewater Analysis

The physicochemical properties of the wastewater (pH, Conductivity, Temperature, Total Dissolved Solid, turbidity, alkalinity and hardness) were determined using standard methods [18]. For heavy metal analysis, the water samples were divided into two portions. The first portions also called wastewater before treatment with TCPF (WBT) were directly treated by adding 2.5 cm$^3$ of concentrated $HNO_3$ to 50 cm$^3$ of each of the wastewater samples in 200 cm$^3$ beakers and digested by heating on a hot plate at 95 $^{\circ}$C until colorless solutions were obtained. The digested samples were cooled and then filtered before raising the volumes to 50 cm$^3$ with deionized water in a 100 cm$^3$ flasks [18]. The concentrations of Lead, Cadmium, Arsenic and Cromium in the wastewater samples were determined using AAS (AA500 PG) [18, 19, 20].

The second portions of the wastewater samples also called wastewater after treatment with TCPF (WAT) were treated with the modified TCPF adsorbent under optimized conditions as determined [8, 14, 21] using 1 g of the TCPF and 20 cm$^3$ of the wastewater in plastic containers. Each mixture was placed on a rotary shaker and shaken at 120 rpm at room temperature (300 K) for a period of 120 min. The mixtures were each filtered using whatman 0.45 filter paper before digestion with $HNO_3$ in the same way the first portions of the wastewater samples were prepared for AAS analysis. After determining the concentration of each of the metal in the two sets of the wastewater samples [8, 14], the percentage adsorption of each metal by the TCPF was calculated using the equation below:

% Adsorption = $\frac{C_a - C_b}{C_a}$ x 100

Where $C_a$ = the concentration of a metal in the wastewater before treatment (WBT), $C_b$ is the concentration of the metal in the wastewater after treatment (WAT).

### 2.2.4 Desorption Studies

The desorption (cleaning) of the used composite adsorbent (TCPF) was carried out with 0.1 M HCl as the cleaning agent. After the adsorption process, 1 g of the used adsorbent was stirred in 100 $cm^3$ of the HCl solution and shaken in a rotary shaker at 120 rpm for 120 min. The solution (supernatant) was filtered. The filtrates were further digested with $HNO_3$ in the same way as the two portions of the wastewater samples were prepared for the determination of metal concentrations by AAS [8, 14, 22].

The percentage desorption for each of the heavy metal was calculated using equation 2 below:

% Desorption = $\frac{C_o - C_e}{C_o}$ x 100

Where $C_o$ = the concentration of the metal adsorbed by the TCPF adsorbent, $C_e$ is the concentration of the metal removed by the 0.1M HCl solution.

### 2.2.5 Statistical Analysis

All analyses were performed in triplicates and the results expressed as mean ± standard deviation (SD). The significant differences in Pb, Cd, As and Cr concentrations before and after lead acid battery recycling wastewater treatment were evaluated using analysis of variance (ANOVA) statistics. A value of $p < 0.05$ at 95% confidence level was considered statistically significant (7, 14, 17].

## 3.0. Results and Discussion

### 3.1 Results

### 3.1.1. Wastewater Analysis

**Table 3.1. Physicochemical analysis of wastewater before and after treatment with TCPF**

| Parameters | WBT | WAT | WHO2011 | NESREA2011 |
|---|---|---|---|---|
| Ph | 2.50 ±003 | 6.75 ± 0.02 | 6.5 - 8.5 | 6 – 9 |
| Temperature (K) | 303 ± 0.20 | 303 ± 0.20 | 294 – 305 | < 313 |
| EC (μS/$cm^3$) | 2163.7 ± 0.16 | 963.7 ± 0.16 | 1000 | 1000 |
| Turbidity (NTU) | 5.0 | 4.5 | 5.0 | < 20 |

| | | | | |
|---|---|---|---|---|
| Total Dissolve Solids (mg/L) | 895 ± 0.01 | 895 ±0.01 | 1000 | 2000 |
| Total Suspended Solids (mg/L) | 157.20 ± 0.15 | 155 ±0.21 | - | 1000 |
| Total Solids (mg/L) | 1002 ± 0.12 | 1000 ±0.09 | 2000 | < 2000 |
| Total Alkalinity (mg/L) | 23 ± 0.00 | 25 ±0.00 | 200 | 200 |
| Total Hardness (mg/L) | 105.01 ± 1.23 | 94 ±0.42 | 100 | 100 |

**Key:** EC: Electrical conductivity, WBT= wastewater before treatment, WAT= Wastewater after treatment. All values for WBT and WAT are Mean of triplicate determinations. The mean values showed significant difference at 0.05 level ($P < 0.05$) between WBT and WAT for each the parameter.

### 3.1.2. Heavy Metal Analysis

**Table 3.2. Heavy metal composition of wastewater before and after treatment with TCPF**

| Heavy Metal | WBT | WAT | % Adsorption by TCPF | WHO2011 | NESREA2011 |
|---|---|---|---|---|---|
| Pb (mg/L) | 8.833 ± 0.02 | 0.007 ± 0.01 | 99.92 | 0.01 | 0.01 |
| Cd (mg/L) | 0.163 ± 0.11 | 0.003 ± 0.01 | 98.16 | 0.003 | 0.005 |
| Cr (mg/L) | 1.596 ± 0.03 | 0.045 ± 0.02 | 97.18 | 0.05 | <1 |
| As (mg/L) | 0.015± 0.04 | 0.010 ± 0.03 | 33.3 | 0.01 | 0.01 |

Key: WBT= before wastewater treatment, WAT= after wastewater treatment. All values for WBT and WAT are Mean of triplicate determinations. The mean values showed significant difference at 0.05 level ($P < 0.05$) between WBT and WAT for each the metals.

### 3.1.3. Desorption studies of the TCPF adsorbent

**Table 3.3. The desorption efficiency of the TCPF for the Metals in the wastewater**

| Metal | Adsorbed by TCPF (mg/L) | Desorbed with 0.1M HCl (mg/L) | % Desorption |
|---|---|---|---|
| Pb | 8.826 | 6.778 | 76.8 |
| Cd | 0.982 | 0.863 | 90.6 |

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| | | | |
|---|---|---|---|
| Cr | 1.551 | 1.246 | 80.3 |
| As | 0.005 | 0.0047 | 94.4 |

## 3.2 Discussion

### 3.2.1 Physicochemical Analysis of wastewater before and after treatment with TCPF

The results of the physicochemical analysis of the wastewater samples before (WBT) and after treatment (WAT) are presented in Table 3. 1. A change in the mean pH of wastewater before treatment (2.50 ± 0.03) and after treatment (6.75±0.02) with the TCPF was observed. This indicated that the wastewater was acidic, which might be due to the use of concentrated acid in car batteries production [16]. The change in pH after treatment with TCPF adsorbent could be associated with the alkaline treatment involved in the preparation of the composite adsorbent [8]. The value was within the permissible limit set by the standard of WHO [23] and NESREA, [24]. The mean temperature of wastewater (303 ± 0.20K) did not change after treatment and was within the WHO [23] and NESREA [24] recommended limits of 294-305 K and 313 K respectively. There was a significant decrease in the electrical conductivity (EC) of the wastewater from 2163.7 ± 0.16 µS/cm before treatment to 963.7 ±0.16 after treatment. The initial high mean value of the EC might be due to high concentration of ionic salts (cations) present in the wastewater sample [16], while the low value observed after treatment could be due to the adsorption of some of the cations by the modified TCPF adsorbent WHO [23] and NESREA [24]. The mean values for total alkalinity of wastewater before and after treatment are within the WHO [23] and NESREA [24] permissible limit of 200 mg/L [16, 17]. A decrease in the total hardness was observed from 105.01+1.23 in wastewater to 94 ± 0.42 after treatment with the TCPF composite which falls within the WHO and NESREA standards

### 3.2.2. Heavy Metal Composition of Wastewater before and after treatment with TCPF

The concentrations of the heavy metals (Pb, Cd and Cr) analysed in the samples of the wastewater before treatment (WBT) and after treatment (WAT) with TCPF adsorbent are presented in Table 3.2. Similarly, the table also contain the percentage adsorption for each of the heavy metals analysed. The mean values for the metals in the wastewater followed Pb >Cr >Cd >As trend, while for the treated wastewater, the trend of Cr>As>Pb>Cd was observed. The values for all the metals in the wastewater before treatment (WBT) were higher than their corresponding values in the wastewater after treatment (WAT) with the TCPF adsorbent and the difference was significant at $p < 0.05$. Similarly, the values were also above the standards set by WHO [23] and NESREA [24]. On the contrary, the values for all the metals in the wastewater after treatment with TCPF were very low and were also within the standards. The low values recorded for the metals in the treated wastewater could be attributed to the excellent performance of the TCPF in heavy metal adsorption. However, the adsorption ability of the TCPF for the metals followed the trend of Pd

>Cr >Cd >As, as shown in the table (3.2). The TCPF adsorbent showed good adsorption behaviour for Pd, Cd and Cr, as the percentage adsorption for each was above 90, while the adsorption for As was as low as 33.33%.

### 3.2.3 Desorption studies

The result for the desorption studies on the TCPF composite used for the adsorption of the heavy metals in the wastewater with 0.1M HCl solution is presented in table 3.3. The results showed high desorption efficiency of the TCPF for all the metals and the percentage recovery were 76.8% for Pb, 90.6% for Cd, 94.4% for As and 80.3% for Cr. Arsenic had the highest value for the percentage desorption. The trend of metal regeneration from TCPF follows: As > Cd > Cr > Pb. This could be associated with the fact that As has the smallest cationic size of (1.18 nm) rather than Pb (1.75 nm), Cd (1.36 nm) and Cr (1.48 nm) [21, 25]. This is a good indication that the TCPF adsorbent can be cleaned and be used again in the removal of the heavy metals.

## 4.0 Conclusion

In this research work, the modified feldspar composite (TCPF) adsorbent was prepared from feldspar and *Theobroma cacao* pods by the calcination method using NaOH as activation agent. The wastewater samples were collected from a pond where lead-acid battery recycling centre discharges its wastewater. After treatment with TCPF adsorbent, Pb, Cd and Cr and As levels in the wastewater were reduced to be within WHO and NESREA permissible limits. The ANOVA test revealed significant difference between the heavy metal levels before and after wastewater treatment at $p< 0.05$. The TCPF adsorbent showed some level of high regeneration/cleaning efficiency with 0.1 M HCl. The results indicated that TCPF has high cation exchange capacity, good adsorption performance for the selected heavy metals, easy cleaning tendency and low-cost. Therefore, TCPF can be considered as an excellent adsorbent for heavy metals in wastewater treatment. This is a crucial progress in the field of adsorption science particularly in wastewater treatment using mixtures of different types of readily available naturally occurring adsorbents.

## Recommendations

It is recommended that the appropriate regulatory agencies at the Local, state and Federal levels in Nigeria should ensure the prohibition of direct discharge of wastewater to water bodies is observed by the industries. Pre-treatment processes such as off stream storage and bankside filtration should be adopted as part of the immediate control measures. Similarly, regular assessment of the waste waters to ascertain their levels of contamination should be emphasized. Since Lead, Cadmium and Chromium and Arsenic are not the only heavy metals that have health effects, there is the need for further research on the ability of TCPF to adsorb other heavy metals in both aqueous solutions and in wastewater bodies. For real scale application, column adsorption studies should be carried out for possible Industrials application of the TCPF.

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