Adsorption of Heavy Metals from an Aqueous Solution Using Activated Carbon Prepared from Ripe and Unripe Plantain Peels

Modupe Elizabeth Ojewumi[1]*, Emmanuel Omotayo Ojewumi[2], Odunlami Abosede Olayemi[3], Princess Gladys Ubong[3], Kayode Joshua Jolayemi[3]

[1] Department of Civil and Environmental Engineering
  FAMU-FSU College of Engineering, Tallahassee, FL 32310, USA

[2] Department of Food Science and Technology
  Federal University of Technology, Akure, Ondo State, P.M.B. 704, NIGERIA

[3] Covenant University, Canaan Land, KM 10, Idiiroko, Sango Ota, Ogun State, P.M.B. 1023, NIGERIA

*Corresponding Author: modupe1.ojewumi@famu.edu
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Abstract

Heavy metals are poisonous and pollute water bodies, posing human health concerns. This research focuses on removing heavy metals from water through adsorption using activated carbon prepared from ripe (RPP) and unripe plantain peels (UPP). This research revealed that the removal efficiencies were higher for ripe plantain peels (about 99.5%) than the unripe peels in the three heavy metal simulated aqueous polluted samples. The adsorption was favorable using the constants developed from the Isotherms, and the Freundlich isotherms fitted the experimental data better than the Langmuir isotherms. The Scanning Electron Microscope (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR) observations revealed the presence of heavy metals on the adsorbent. It was established that activated carbon prepared from ripe and unripe plantain peels is an effective, economical, environmentally friendly, and cheap natural adsorbent for removing heavy metals from polluted water.

1. Introduction

The exponential growth in agricultural and livestock waste, which endangers the lives of living and non-living things, has compelled the need to study how they could be reused [1]. A lot of work has been done by researchers on various ways by which waste can be of positive relevance to guarantee a healthier environment, such as the bioconversion of waste paper to ethanol and glucose, potatoes and citrus peel to biodiesel [2]. Agricultural (biomass) and household wastes can be useful if properly recycled [3-5]. When this waste is not properly managed, it can become a serious environmental problem [6,7]. Alternative means by which solid wastes are treated include incineration [8] and landfilling [9], which are not eco-friendly. The chemical procedure involves using inorganic acids such as sulphuric [10] and hydrochloric acids [11] in hydrolysis. This is an expensive method and not environmentally friendly; the resulting acid solution is difficult to recycle for further use on other cellulolytic waste materials available [12]. Environmental pollution may not directly affect the economy but adversely affects the human population, especially in the health sector [13,14].

Water is in high demand and becomes highly valuable as the world's population grows rapidly [15]. Heavy metal contamination is a serious threat to the worldwide ecosystem. Heavy metals such as copper, iron, nickel, and lead, among others, have been released in large quantities into the atmosphere due to rapid industrialization

[16]. Many businesses, such as metal plating, mining, and tanneries, discharge heavy metal-contaminated effluent into the environment. It is generally understood that some metals can have harmful or hazardous effects on humans and the environment [17]. Unlike organic wastes, these metals are non-biodegradable and can accumulate in living tissues, producing a variety of illnesses. Chemical precipitation, ion exchange, membrane, filtration, and activated carbon adsorption are all methods for removing heavy metals from water. These techniques, however, are either costly or have additional drawbacks, such as excessive energy consumption and inefficiency when heavy metals are present in low concentrations [18]. Adsorption is a physio-chemical treatment procedure that is demonstrated to be successful in removing heavy metals from aqueous solutions. According to a recent study, adsorption technology is widely used in industry. Activated carbon is the most extensively utilized material for adsorption. Despite their usefulness in treating water, carbon adsorbents are still expensive. As a result, using affordable resources to produce activated carbon has been promoted [19,20]. Heavy metals are naturally occurring elements with an atomic number of more than 20, high density and melting point (at least 5 g/cm^3), and can be poisonous even at low doses. They are naturally found in various surroundings, major structures, and artificial mixtures [21].

Heavy metals are often found in trace levels in natural water sources, but many are toxic, even in small amounts. The rising number of heavy metals in our resources raises concerns, especially because many industries dump metal-containing wastewater into water bodies without treating them appropriately [22].

In recent years, environmental contamination caused by these metals has become a growing environmental and public health issue. Furthermore, human exposure has grown significantly due to an exponential development in their usage in a range of industrial, agricultural, residential, and technological applications. They are widely disseminated in the environment due to their various industrial, household, agricultural, medicinal, and technological applications, raising concerns about their potential impacts on human health and the environment [23]. Adsorption is when gas or liquid accumulates on the surface of another solid object in the form of molecules, atoms, or ions. It is also a physical or chemical connection of material molecules in the active sites of a surface by the weak Vander Waals force or by establishing chemical bonds with the surface's effective sites [21]. This research aims to remove heavy metals from water through adsorption, using activated carbon prepared from Ripe and Unripe Plantain Peels.

1.1 Mechanism of Adsorption

Adsorption occurs because the adsorbent's surface particles are not in the same environment as the particles within the bulk. Inside the adsorbent, all forces acting between the particles are mutually balanced. Still, on the surface, the particles are not surrounded on all sides by atoms or molecules of their kind, and thus they have unbalanced or residual attractive forces [24,25]. All solid substances have the capability to attract to their surface molecules of solutions or gases with which they are contacted, which is called adsorption [26-28].

1.1.1 Langmuir Isotherm

The Langmuir equation, developed to explain gas-solid phase adsorption, is also used to compare and evaluate the adsorptive capacity of different adsorbents. The Langmuir isotherms adjust the adsorption and desorption rates to account for surface coverage [29]. The linearized form of the Langmuir equation is presented in Eq. 1.

$$\frac{Ce}{qe} = \frac{1}{qmKe} + \frac{Ce}{qm}$$

(1)

Where Ce stands for the equilibrium adsorbate concentration (mg/g). K_L is a Langmuir constant related to adsorption capacity (mg/g). It may be related to differences in the suitable area and porosity of the adsorbent, suggesting that adsorption capacity will be greater when the surface area and pore volume are large. RL is a dimensionless constant expressing the Langmuir isotherm's fundamental properties. It is written as in Eq. 2.

$$L = \frac{1}{1+KL\,Co}$$

(2)

1.1.2 Freundlich Isotherm

The Freundlich equation was developed to offer an experimental description of the change in adsorption heat as a function of the adsorbate concentration (vapor or solute) on an energetically heterogeneous surface. The relationship for the Freundlich isotherm is given as in Eq. 3.

$$\log qe = \log KF + \frac{1}{n}\log Ce$$

(3)

K_F denotes adsorption capacity (L/mg), and 1/n denotes adsorption intensity, energy distribution, and adsorbate site heterogeneity [22]. This project aims to remove heavy metals from water through adsorption, using activated carbon prepared from plantain peels.

2. Materials and Methods

2.1 Adsorbent Preparation and Characterization

Ripe and unripe peels were collected from Cafeteria 2 in Covenant University, Ota, Nigeria. Both peels were treated independently but in the same way. The peels were chopped into little fragments to remove unwanted dirt and rinsed with distilled water several times. The materials were then air-dried for 24 hours before oven-drying at 100 °C for another 8 hours [30,31]. The peels were later pulverized and sieved using a sieve with particle sizes ranging from 150 to 425 micrometers. The morphological structures of the produced adsorbent were analyzed using SEM (Thermo Fisher Scientific's Apreo 2 SEM), and the functional groups were identified by FTIR (Bruker's Tensor II FTIR).

2.2 Sample Preparation for SEM and FTIR

SEM, Thermo Fisher Scientic's Apreo 2 SEM at 150 kV accelerated voltage, and 10–15 mm working distance was used to assess the morphological characterization of the particles. Gold-coated samples were prepared before their introduction into SEM characterization cell [32].

As for FTIR, finely ground samples were missed with potassium bromide (KBr) powder in a ratio of about 1:100, and placed into a pellet press with applied pressure (around 10 tons) to form a transparent pellet. The samples were placed in a pellet in the sample holder of the FTIR spectrometer for analysis. Samples were evenly distributed, and accurate spectral analysis was performed.

2.3 Impregnation and Carbonization of Adsorbent

The adsorbents were put into a muffle furnace and carbonized at 400 °C for 1 hour. They were allowed to cool down and then impregnated using 0.2 M sulphuric acid with a ratio of 1 g of adsorbent to 10 ml acid for 24 hours. After this, the mixture was filtered and washed several times until it became neutral. The adsorbent was dried in an oven for 2 hours at 110 °C. The dried adsorbent was then placed and put into sample bottles pending adsorption [20].

2.4 Adsorbent Experiment

The solutions were made separately from a 1000 ppm analytical-reagent grade $CuSO_4$, $NiCl_2$, and $ZnCl_2$ standard solution. To make the heavy metal solution, each metal solution was produced according to the concentration necessary (20, 30, 40, 50 mg/l) and then combined together [20,33]. Activated plantain peel was added to the metal solutions. The mixture was stirred to allow adsorption to occur. After adsorption, the mixture was filtered to separate the peels from the solution. The concentration of heavy metals in the filtrate is measured.

2.5 Efficiency of Removal of Heavy Metals from the Treated Water Sample

The removal efficiency or the Adsorption capacity is calculated as in Eq. 4, where Co is the initial concentration, and Ce is the final concentration.

$$Removal\ Efficiency\ (\%) = \frac{Co - Ce}{Co} x\ 100 \tag{4}$$

3. Results and Discussions

3.1 Physical Characterization of Adsorbent

Different particle sizes ranging from 150 to 425 μm were used to evaluate the effect of particle size. Fig. 1(a) and Fig. 1(b) show that an increase in the particle size led to a decrease in the removal efficiency. This is because the greater the particle size, the lesser the surface area of the adsorbent and, subsequently, the lesser active sites available for the adsorption of heavy metals from the simulated wastewater sample. This result perfectly harmonizes with the literature [15]. Therefore, increasing particle size will decrease the efficiency of removing heavy metals. The graphs showed a better fit for unripe plantain peels, as their lines of best fit had a greater R^2 value. However, the removal efficiency is higher for RPP than for UPP for the plot of removal efficiency against particle size for all the 3 simulated heavy metal aqueous solutions.
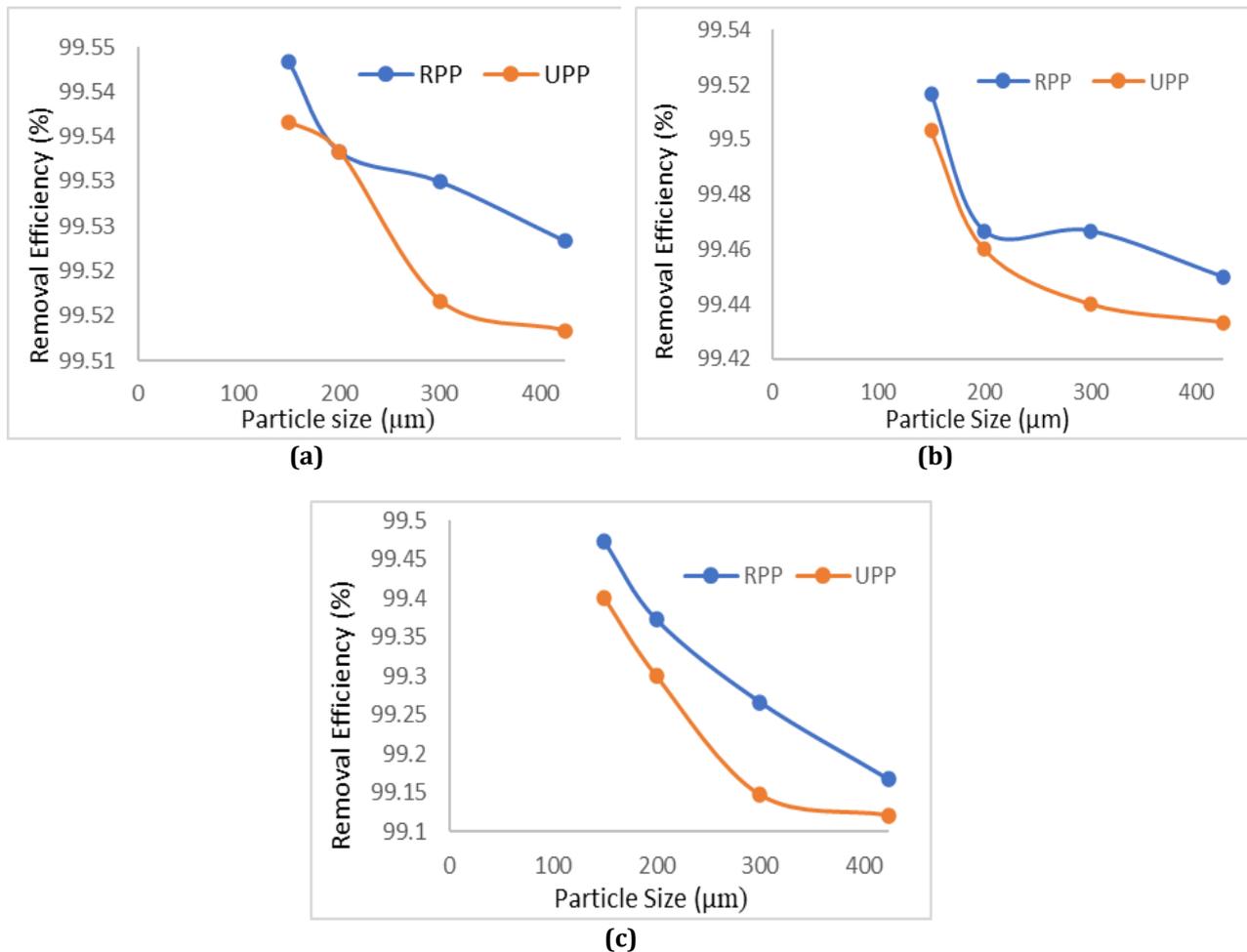
Fig. 1 *Removal efficiency against particle size (a) Copper; (b) Nickel; & (c) Zinc*

3.2 Effect of Contact Time

For the contact time, both adsorbents were studied at contact times of 30, 60, 90, and 120 minutes, respectively, while keeping the particle size, adsorbent dose, and metal ion concentration constant. Fig. 2 shows that an increase in contact time led to an increase in the removal efficiency of both adsorbents. This means that at higher contact time, the adsorption capacity of both adsorbents increased. Maximal adsorption was achieved at 120 minutes, while minimal adsorption was achieved at 30 minutes for both adsorbents. The higher the contact time between the surface of the adsorbents and the metal ions in the solution, the more time is allowed for the adsorption and equilibrium to occur [34]. However, the RPP gave a better and more accurate line of fit for all three metal ions [33].
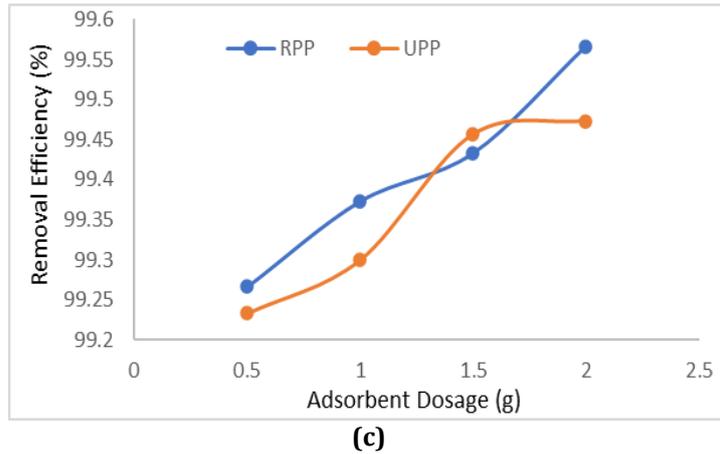
3.3 Effect of Adsorbent Dosage

For the variation of adsorbent dosage, the adsorbents were added in doses of 0.5, 1.0, 1.5, and 2.0 g, respectively (Fig. 3). An increase in the mass of adsorbent added led to an increase in the removal efficiency because an increase in dosage leads to an increase in the total surface area of the adsorbent, making more sites available for the adsorption of the heavy metals to take place. Maximum adsorption of both ripe and unripe plantain peels was achieved at an adsorbent dose of 2 g, while minimum adsorption was achieved at 0.5 g for all the heavy metal ions due to a lack of active binding sites. Therefore, an increase in adsorbent dose makes available more active binding sites for the adsorption of heavy metals. This result is coherent with the literature [34,35]. However, the ripe plantain peels had a better line of fit than unripe plantain peels and hence, maximal adsorption would be better achieve using a high dose of activated carbon prepared from ripe plantain peels.

(a)

(b)

(c)
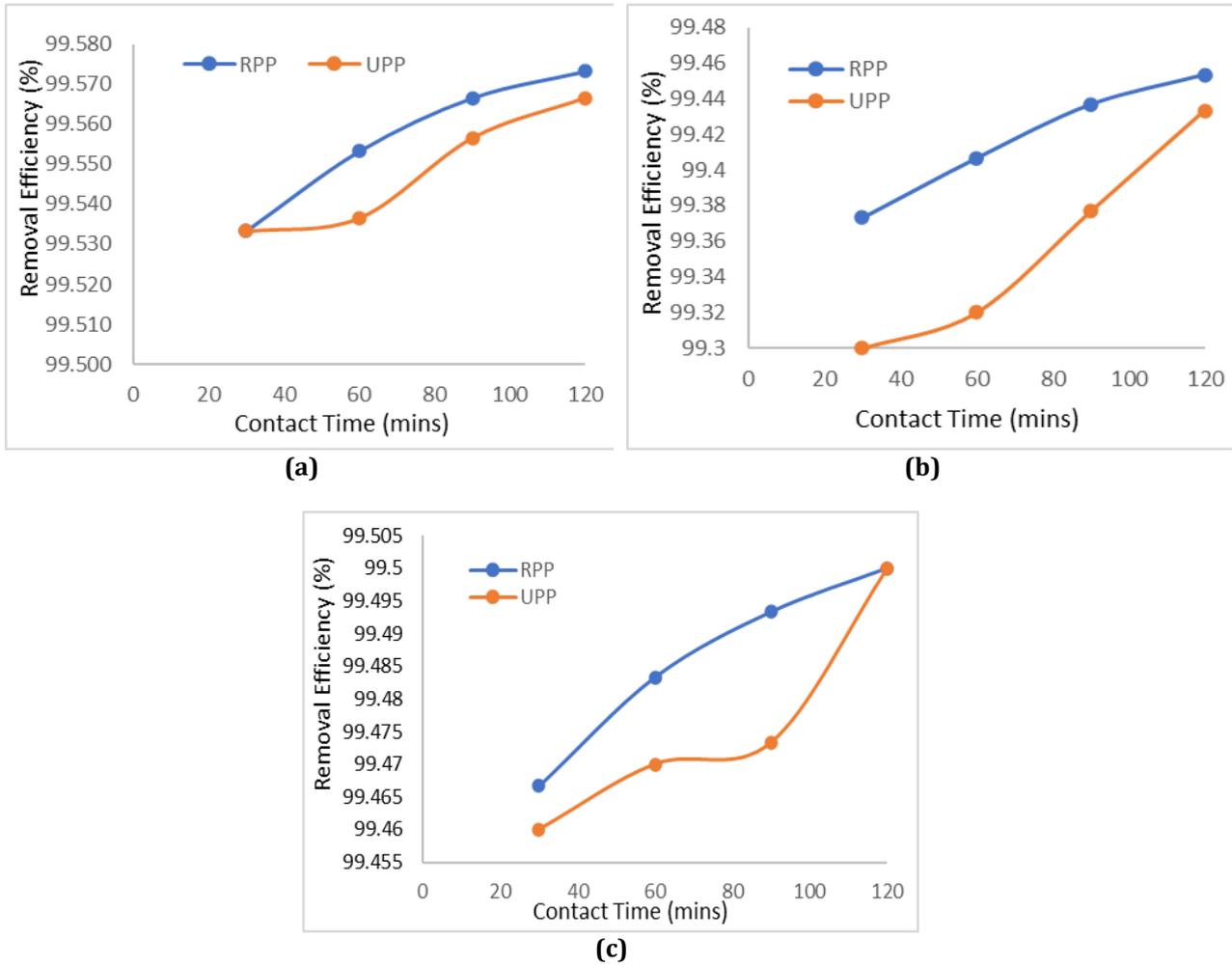
Fig. 2 *Removal efficiency against contact time (a) Copper; (b) Nickel; & (c) Zinc*


(a)

(b)

(c)
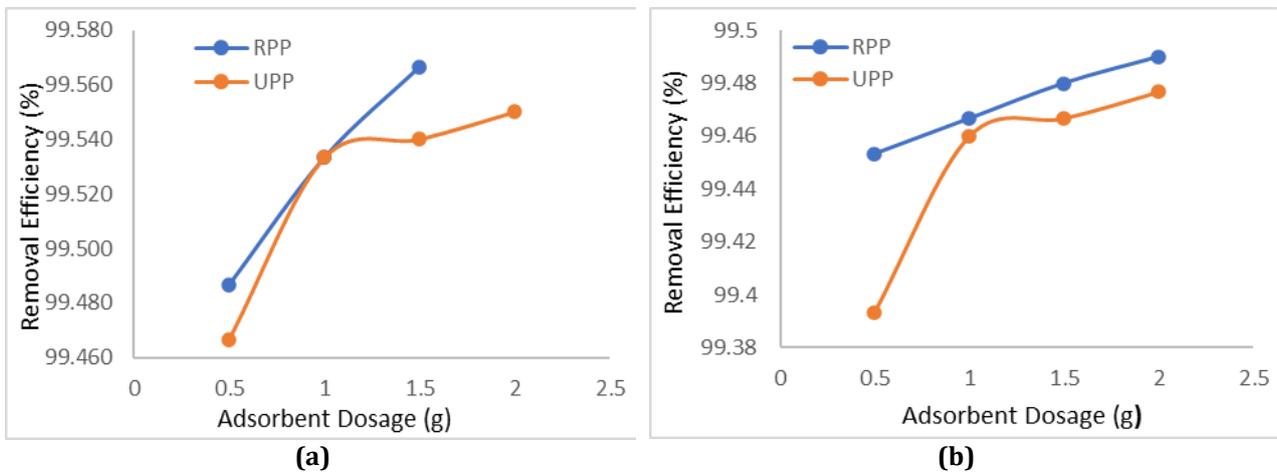
Fig. 3 *Removal efficiency against adsorbent dosage (a) Copper; (b) Nickel; & (c) Zinc*

3.4 Effect of Initial Metal Ion Concentration

Fig. 4, it is obvious that there was a decrease in the removal efficiency of all heavy metals from the water as the concentration of these heavy metals was increased in the simulated wastewater sample. This trend results from saturation that occurs in the adsorption or binding sites because, at lower concentrations, all the metal ions present can mingle conveniently with the binding sites. At a higher concentration, all the metal ions present will not be able to interact conveniently with the binding sites, hence the reason for the lower removal efficiency [36]. The graphs showed a more accurate line of fit for RPP, indicating that RPP is better suited for the adsorption of heavy metals from water.

(a)

(b)

(c)
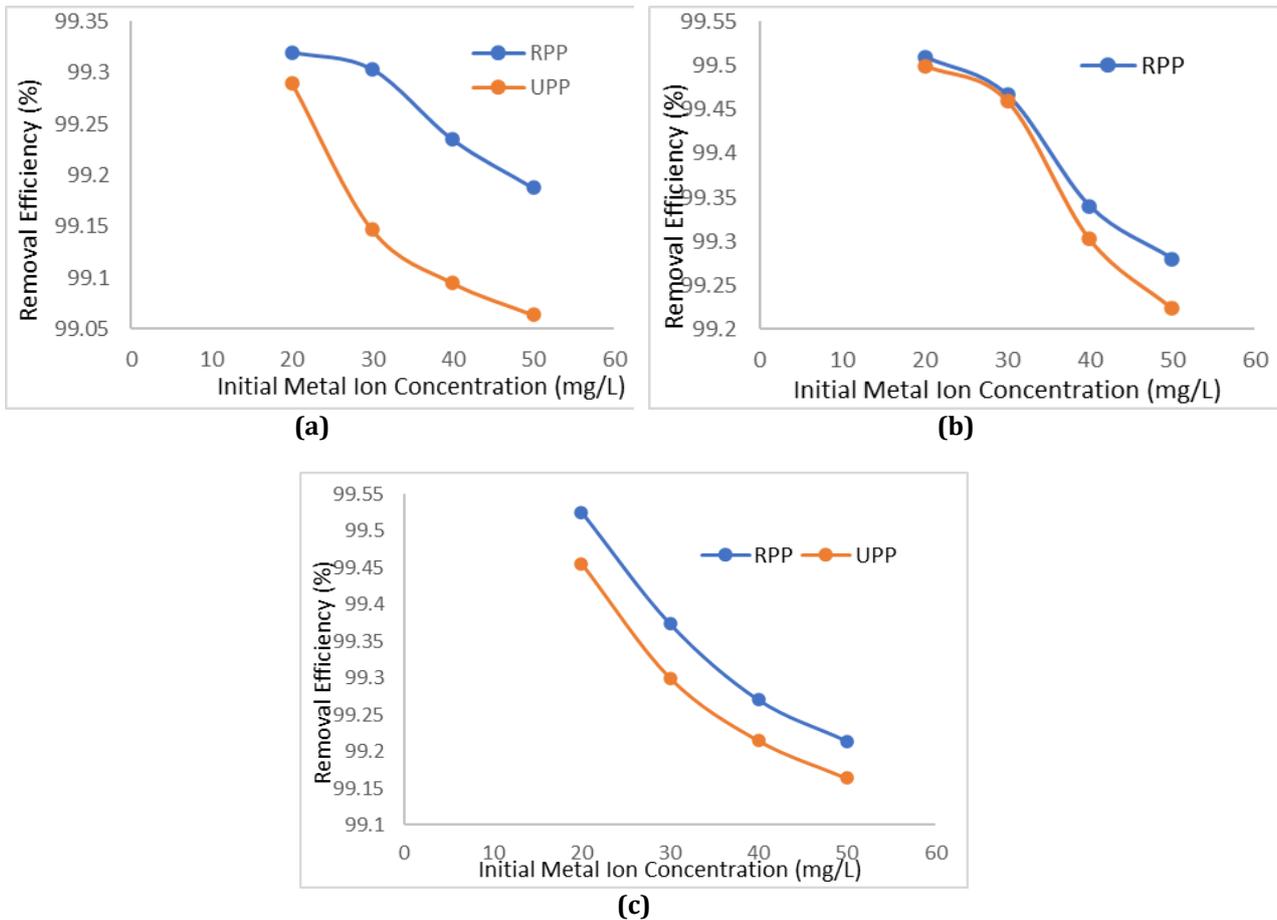
Fig. 4 *Removal efficiency against concentration (a) Copper; (b) Nickel; & (c) Zinc*

3.5 Effect of Initial Metal Ion Concentration

3.5.1 Langmuir Isotherm

The Langmuir adsorption isotherm assumes that adsorption occurs on a homogeneous site and that adsorption stops when sites become unavailable [36]. The adsorbent correlation coefficient (R^2) indicates that monolayer adsorption is perfectly matched. This indicates that the adsorption sites are energetically and structurally identical, implying no interaction between the molecules adsorbed and adjacent sites. Due to the surface of the sites, the adsorbate cannot be transported from one accessible site to another, and the plantain peel has a limited adsorptive capacity for metal ions [36,37]. The R^2 values of the Langmuir isotherm for all metal ions are greater for the RPP than the UPP. This shows that the RPP is a better adsorbent than UPP. Also, the R_L values for all the isotherms ranged from 0.0281 to 0.0795, which are greater than 0 but less than 1, indicating favorable adsorption and proving that the Langmuir isotherm fits the experimental data perfectly (Fig. 5).

3.5.2 Freundlich Isotherm

Fig. 6 shows the correlation coefficient values of the linearized equation of the Freundlich model for the adsorption of copper ion was 0.9944 for UPP, and 0.973 for RPP, zinc and nickel following the same trend, with the Ripe plantain peels having a higher R^2 value than the Unripe plantain peel, showing that the RPP is also better suited for the Freundlich model than the UPP. The Correlation coefficient values for removing the three metal ions using the two adsorbents were also much higher than those of the Langmuir model at the same conditions [38].
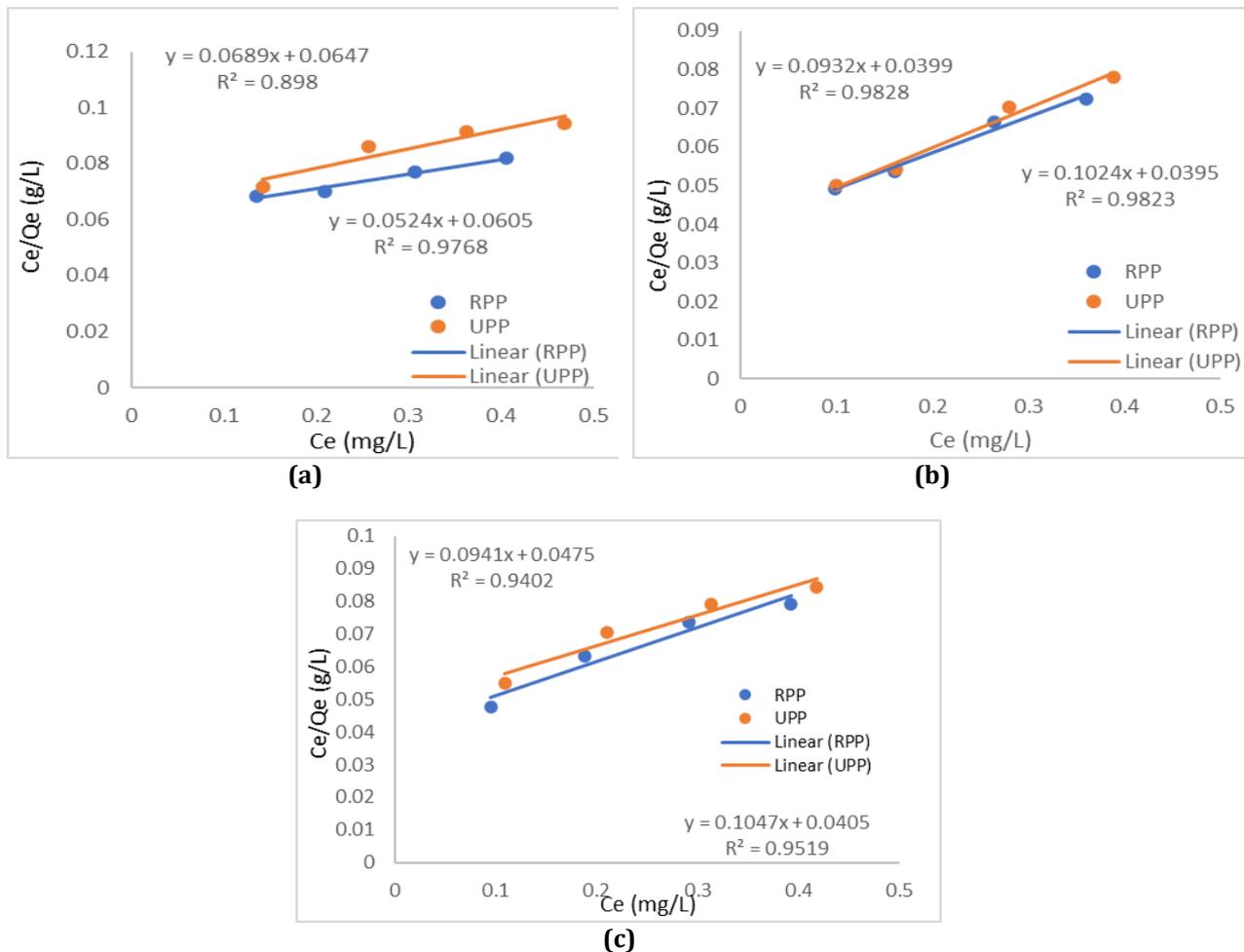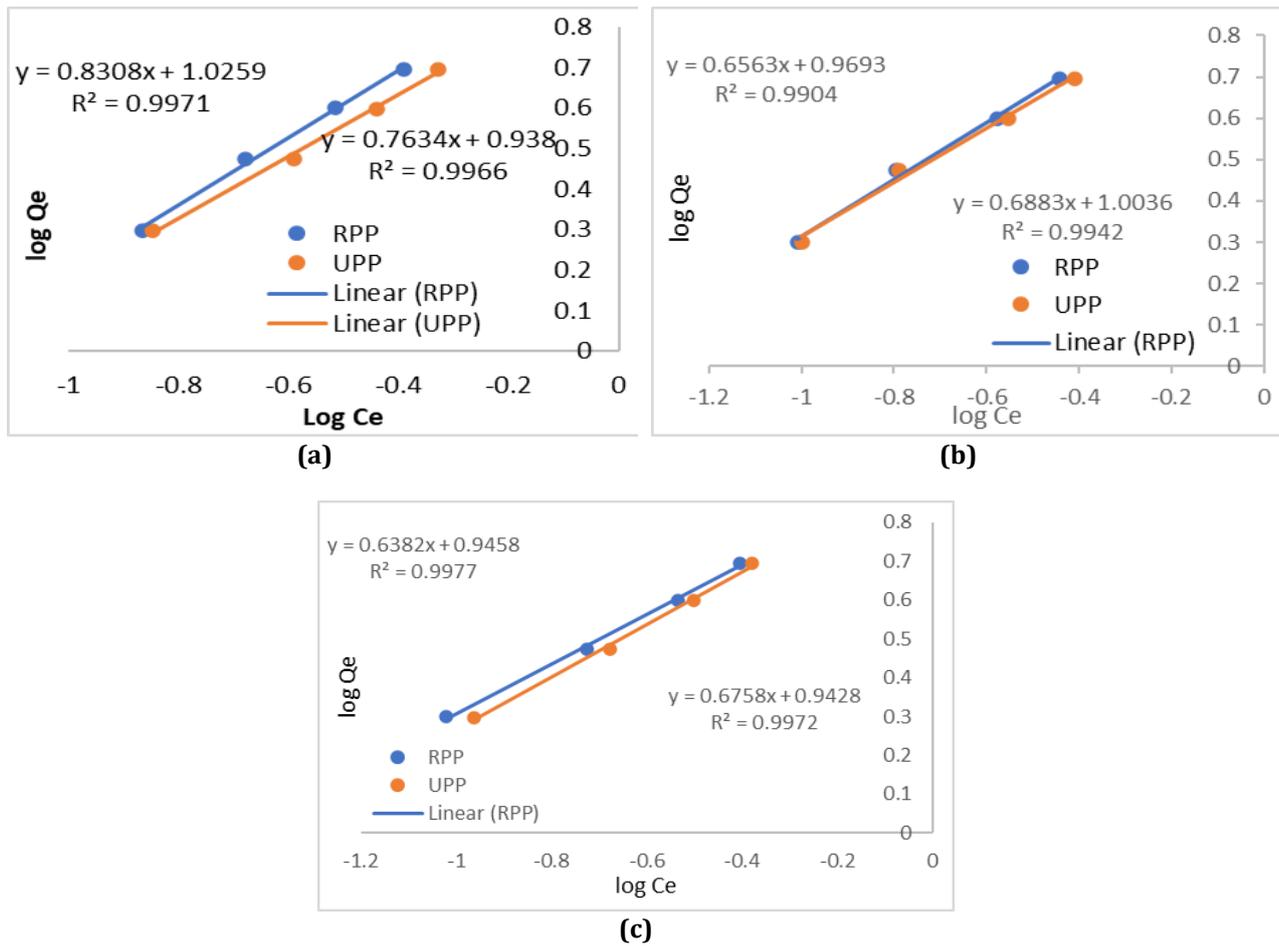

Fig. 5 *Langmuir isotherm for removal of (a) Copper; (b) Nickel; & (c) Zinc*

(a)

(b)

(c)

Fig. 6 *Freundlich isotherm for removal of (a) Copper; (b) Nickel; & (c) Zinc*

3.6 SEM Analysis

Fig. 7 shows the surface morphology and structure of the plantain peels observed by the Scanning Electron Microscope (SEM). The microporous structure was observed at a magnification of 9000x. The original peels have a highly porous structure and, therefore, can take up more particles, and in this case, metal ions. The large volume of pore spaces in the micrographs of both RPP and UPP before adsorption explains the high removal efficiency of both adsorbents [37], as there is much space for the uptake of these metal ions. After adsorption, the SEM images revealed the presence of the heavy metals on its surface. After adsorption, there is a clear agglomeration of particles on the surface of the peels, most especially the ripe plantain peels. The peels were noticed to have a cohering structure with minimal pores. This is evidence that the heavy metal ions were adsorbed into the functional groups on the plantain peels activated carbon.


(a)

(b)

(c)

(d)
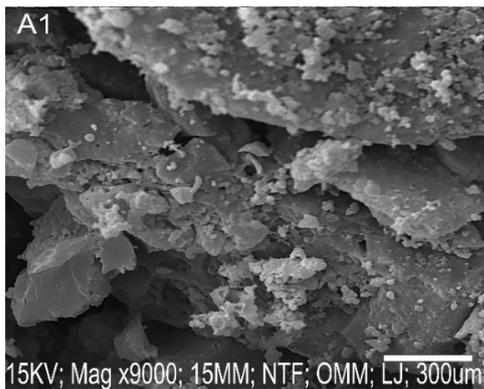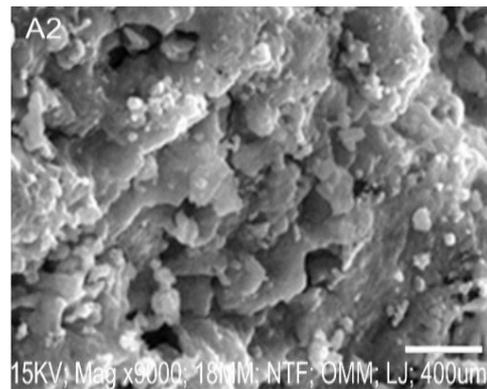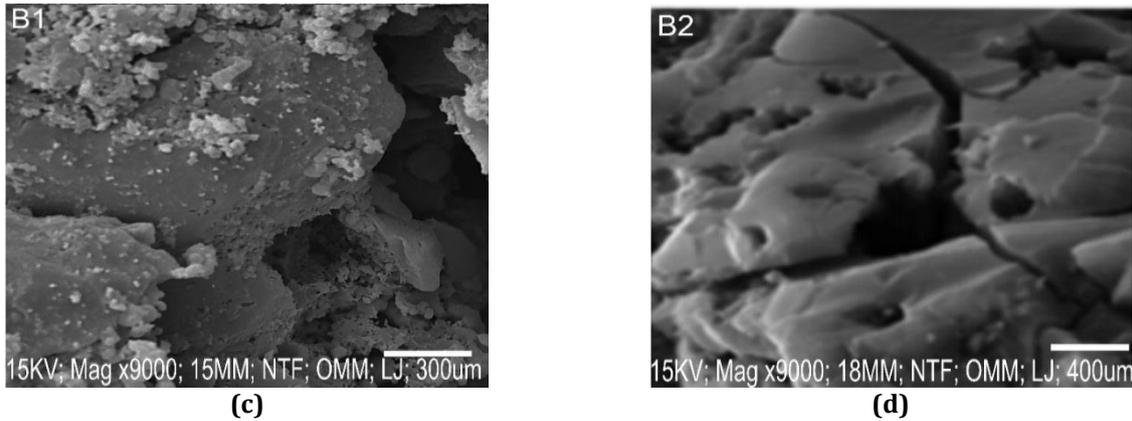
Fig. 7 *SEM images (a) UPP before adsorption; (b) UPP after adsorption; (c) RPP before adsorption; (d) RPP after adsorption*

3.7 FTIR Analysis

The FTIR spectrum of the activated carbon derived from plantain peels reveals the presence of several functional groups that serve as adsorption binding sites for heavy metal ions, Fig. 8. The adsorption spectra found in the activated carbon in Fig. 9 revealed the adsorption peaks that contained the several functional groups that serve as adsorption binding sites for the heavy metal ions. Broad peaks at 3487 and 3480 cm^{-1} correspond to the stretching vibrations of strong O-H groups. They indicate the presence of free hydroxyl groups on the surface of the activated carbon. These hydroxyl groups can potentially interact with heavy metal ions through hydrogen bonding. Peaks at 2350 cm^{-1} correspond to the Carbondimide group in UPP. Carbondimide groups contain a carbon-nitrogen double bond and are commonly found in amide compounds. This suggests the presence of amide functional groups on the surface of the activated carbon. The peak at 2000 cm^{-1} corresponds to the Ketenimine group in RPP. Ketenimine groups contain a carbon-nitrogen triple bond and are known for their reactivity. This suggests the presence of ketenimine functional groups on the surface of the activated carbon. Presence of amide and amine functional groups: The peaks at 2350 cm^{-1} and the broad peaks at 3487 and 3480 cm^{-1} indicate the presence of amide and amine functional groups, respectively. Amide groups are commonly found in compounds such as proteins and peptides, while amine groups refer to compounds containing the amino group (NH_2). These functional groups can contribute to the adsorption of heavy metal ions through various interactions.

The FTIR spectrum suggests that the activated carbon derived from plantain peels contains functional groups such as hydroxyl groups, amide groups, and amine groups. These functional groups provide binding sites for the adsorption of heavy metal ions, making the activated carbon an effective adsorbent for metal ion removal.

In the FTIR spectra of the activated carbon after the adsorption process, it is clear that some peaks have either shifted, disappeared totally, or new peaks have been formed. There is a decrease in the free hydroxyl content of both RPP, as the peaks reduced from 3487 to 3367 cm^{-1} in UPP and from 3480 to 3479 cm^{-1} in RPP, hence showing that the heavy metal ions took up these sites during the adsorption process, and also show the possible interaction between the heavy metals and the functional groups on the surface of the activated carbon prepared from plantain peels. Results obtained for adsorption in this study agree with the report of [39].
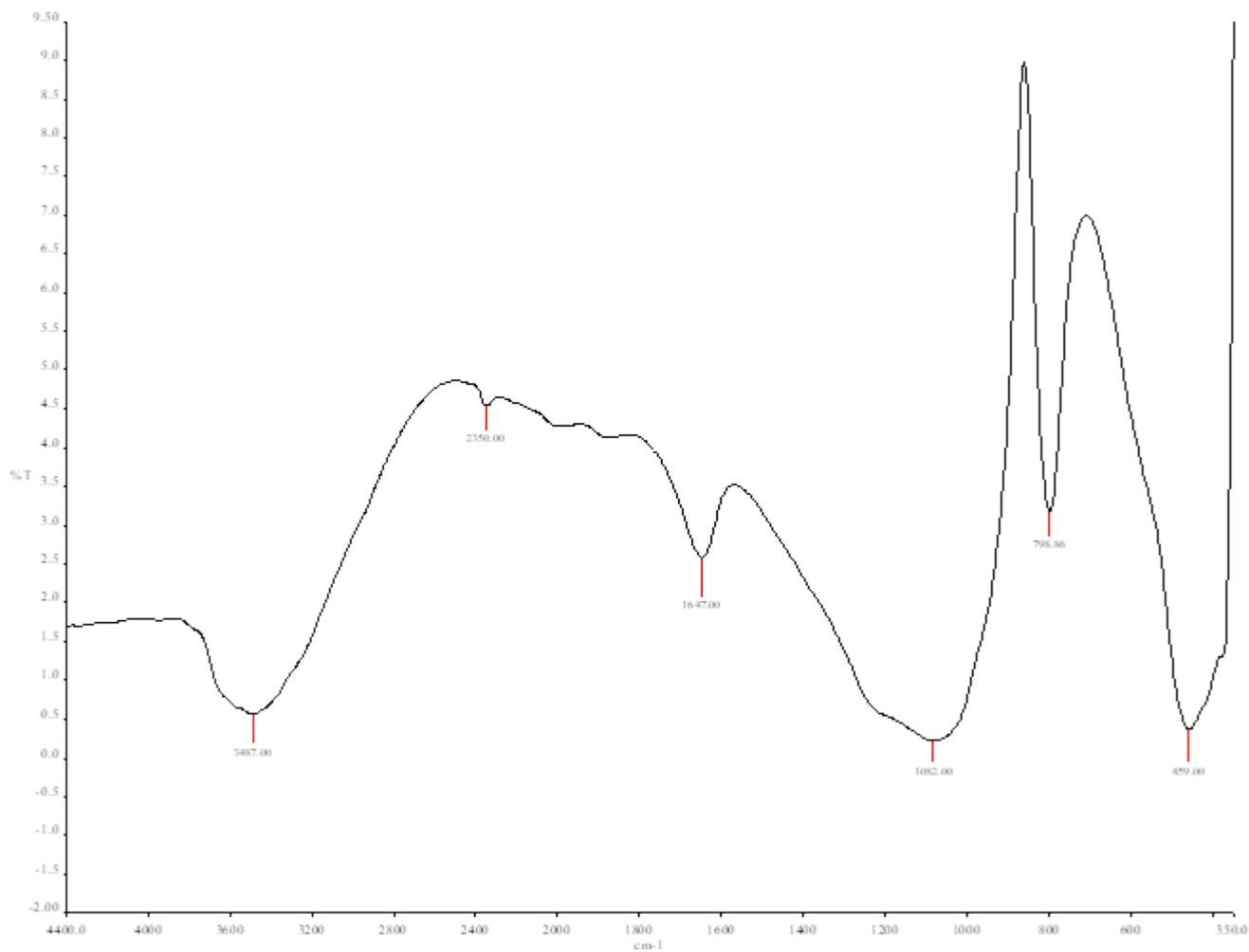
Fig. 8 *UPP before adsorption*
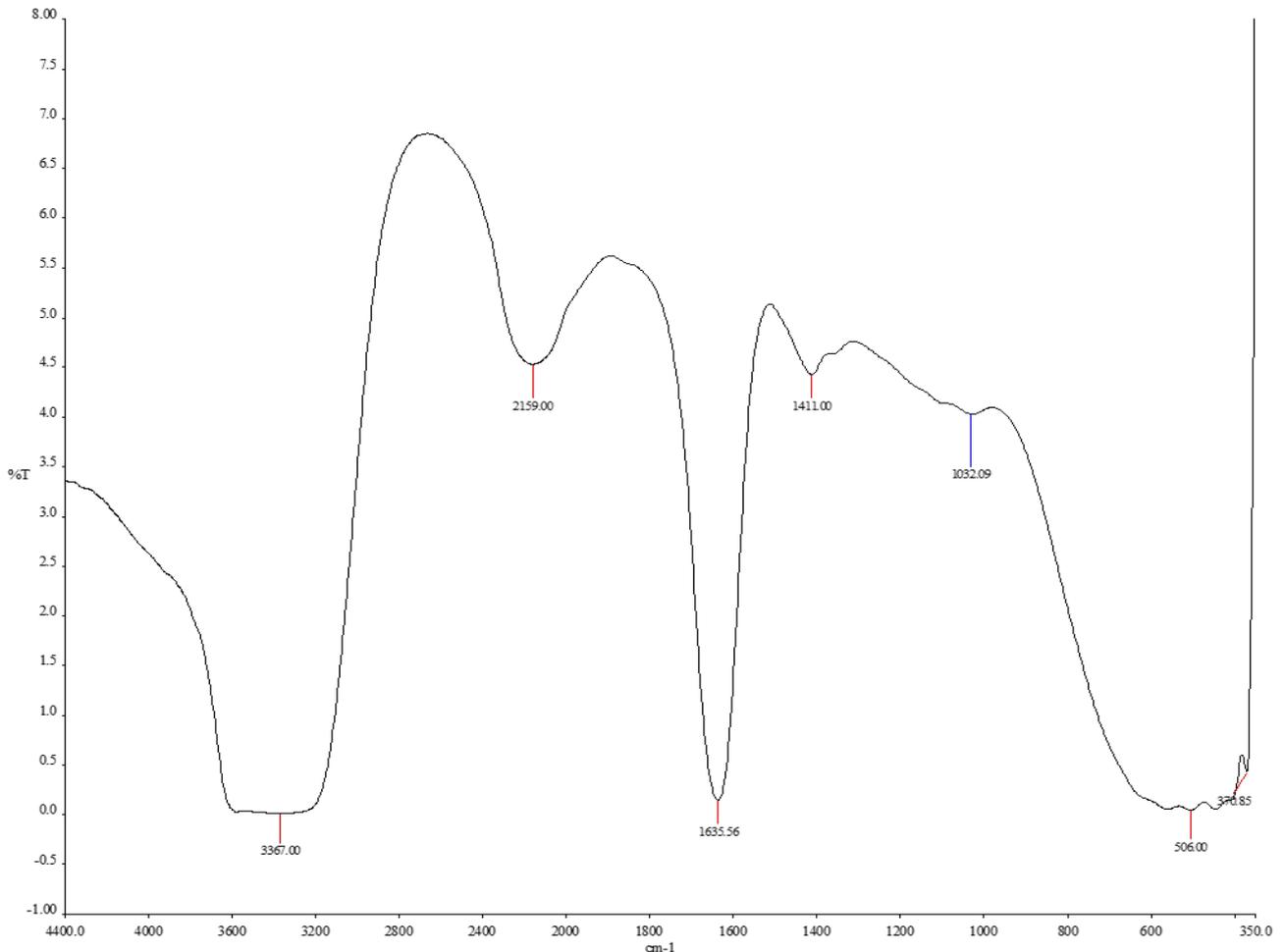
Fig. 9 *UPP after adsorption*

4. Conclusion

This research has shown that activated carbon derived from ripe (RPP) and unripe plantain peels (UPP) is effective for removing heavy metals from water, with ripe peels demonstrating higher removal efficiencies. The maturity of plantain peels significantly influences their adsorption capabilities. Both types of activated carbon are cost-effective natural adsorbents for copper, zinc, and nickel. Increasing contact time and adsorbent dose while decreasing particle size and initial metal ion concentration enhances removal efficiency. The adsorption process follows a multilayer mechanism, best described by the Freundlich isotherm model. R2 values of the Langmuir isotherm for all metal ions are greater for the RPP than the UPP. This shows that the RPP is a better adsorbent than UPP. SEM and FTIR analyses confirmed heavy metal presence on the adsorbent surface, indicating binding to functional groups. Using plantain peel-derived activated carbon offers advantages such as effectiveness, economic viability, environmental friendliness, and low cost. These adsorbents provide a sustainable solution for mitigating heavy metal pollution in water, addressing environmental and health concerns. Further research is recommended to optimize the adsorption process and explore broader applications in water treatment systems, promoting a healthier environment for future generations.

Acknowledgement

Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Penerbit
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Author Contribution

*Modupe Elizabeth Ojewumi: **conceptualized this work and wrote the manuscript**; Emmanuel Omotayo Ojewumi, Odunlami Abosede Olayemi: **Proofread the manuscript**; Kayode Joshua Jolayemi: **Performed the analysis**; Princess Gladys Ubong: **Carried out the experiment**.*

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