Studies on the Removal of Heavy Metal from Incinerator Bottom Ash Using Carbon dot Nanoparticles from Plantain peels (*Musa paradisiaca*)

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Abstract- Incinerator bottom ash (IBA), a by-product of mixed waste combustion, often contains toxic heavy metals that pose significant risks to soil quality, water resources, and human health when indiscriminately disposed into the environment. In this study, carbon dot nanoparticles (CDs) were synthesized from plantain peels using hydrothermal synthesis and characterized by ultraviolet‑visible spectroscopy (UV‑Vis), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and Brunauer‑ Emmett‑Teller (BET) analysis. The CDs exhibited a high surface area of 999.900 m^2/g, a total pore volume of 0.15540 cm^3/g, and an average pore diameter of 3.005 nm, confirming their mesoporous nature. Batch adsorption experiments were performed to assess heavy metal removal from IBA. Results showed outstanding efficiencies: iron (Fe) decreased from 29.141 mg/kg to 0.001 mg/kg within 8 hrs. (480minutes), cadmium (Cd) reduced from 1,561 mg/kg to <0.001 mg/kg after 2hrs of treatment (240 minutes), similarly zinc (Zn) reduced from 1,181 mg/kg to 10.05 mg/kg after 8 hours (480 minutes) of treatment, The copper solution quality reference standard decreased from 2.0 mg/L to 0.08 mg/L after 8 hours (480 minutes) of treatment with carbon dot. The percentage efficiency for the treatment with carbon dot gave 99.99% for iron, 99.99% for cadmium, 99.15% for zinc and 79.1% of copper. Adsorption isotherm analysis revealed that the process followed the Freundlich model, with $n > 1$ indicating favorable adsorption. Kinetic studies demonstrated that Fe and Zn uptake proceeded mainly via physisorption (diffusion-controlled), whereas cadmium removal occurred through chemisorption, attributable to strong interactions between Cd^{2+} and oxygen-containing functional groups (‑OH, ‑COOH, ‑C=O) on the CDs. When compared with the Nigerian Upstream Petroleum Regulatory Commission (NUPRC) permissible limits (Cd: 1.00 mg/kg; Cu: 1.00 mg/kg; Zn: 50 mg/kg), all post-treatment concentrations were below threshold values, while Fe had no defined limit. These findings highlight plantain peel‑derived carbon dots as an efficient, eco-friendly, and sustainable adsorbent for heavy metal remediation from incinerator bottom ash.

Keywords: Incinerator Bottom Ash (IBA); Carbon Dot Nanoparticles; Plantain Peels; Heavy Metal Removal; Freundlich Isotherm; NUPRC permissible limit.

I. INTRODUCTION

The improper disposal of incinerator bottom ash (IBA), a byproduct of municipal solid waste (MSW) incineration, poses significant environmental and public health risks due to its high concentrations of toxic heavy metals such as cadmium (Cd), iron (Fe), copper (Cu), and zinc (Zn). These metals can leach into soil and water, where they undergo bioaccumulation, bioconcentration, and biomagnification through the food chain from contaminated soil and water, to plants, animals, and ultimately humans [1}. The persistence and toxicity of heavy metals make them long-term ecological hazards, as they accumulate in the tissues of living organisms and threaten both environmental integrity and human health [2]. Heavy metals are naturally occurring elements with atomic weights and densities of at least five times greater than that of water. Anthropogenic activities such as mining, smelting, manufacturing, and improper waste disposal significantly elevate their concentrations in the environment [3]. While modern waste management practices only focus in reducing the environmental burden of solid wastes leaving the heavy metals concentrated in the ash. Incineration, which happens to be one of the major strategies for managing municipal solid waste (MSW), reduces waste volume by up to 80–90% [4]. However, the safe management of IBA remains a global challenge due to the risk of heavy metal leaching into the environment if untreated [5]. Over the years, several treatment methods have been developed to mitigate the risks associated with IBA. Early approaches focused on stabilization and solidification. For example, cement-based solidification was applied to immobilize heavy metals in IBA, but the method often increased leachability over time and substantially raised the final waste volume, limiting its large-scale application [6]. To overcome these drawbacks, chemical extraction methods using strong acids such as hydrochloric and nitric acids were introduced, but this generated secondary pollution and required extensive neutralization [7]. Later, thermal treatment techniques were explored to volatilize and separate heavy metals; however, these required high energy inputs and contributed to greenhouse gas emissions [8]. While these conventional methods achieved varying degrees of success, they were associated with limitations in cost, efficiency, and environmental sustainability [9]. Recent advances in remediation strategies have shifted toward nanotechnology-based solutions. Nano-remediation, the application of nanoscale particles (1– 100 nm) for pollutant removal, has gained significant attention due to its high efficiency and environmental compatibility [10]. Among various nanomaterials, carbon dot nanoparticles (CDs) are particularly promising. Unlike general nanoparticles, CDs are ultrasmall particles ranging from 1–10 nm, possessing high surface area and abundant functional groups that enhance their adsorption capacity for heavy metals [11]. Biomass-derived CDs represent an eco-friendly and cost-effective alternative for pollution control. In particular, plantain peels—a rich carbonaceous agricultural waste—have been identified as a viable precursor for CD synthesis [12]. Their application offers a sustainable and low-cost approach for IBA remediation, potentially overcoming the drawbacks of conventional treatment techniques [13].

II. MATERIALS AND METHODS

Materials

The following materials were collected for this study: Incinerator bottom ash (IBA), Plantain peels, and Distilled water.

The collection of incinerator bottom ash was carried out using hand gloves, a nose mask, polythene bags, a stainless-steel shovel, a spatula, and a plastic container. Plantain peels, the raw material for the synthesis of carbon dot nanoparticles, were collected from local fruit vendors, thoroughly washed with distilled water to remove adhering dirt, and sun-dried prior to use. The laboratory apparatus employed during the study included beakers, measuring cylinders, Petri dishes, and glass rods.

Analytical grade reagents were employed throughout the study to ensure accuracy and reliability of results. The chemical reagents used for this study are presented in Table 1.

Table 1: Chemicals reagents used for the study

Name	Supplier	Manufac turer	% purity
Hydrofluoric acid (HF)	Thermo Fisher Scientific	Thermo Fisher	48%
Nitric Acid (HNO3)	Thermo Fisher Scientific	Thermo Fisher	65%
Perchloric acid (HClO4)	Thermo Fisher Scientific	Thermo Fisher	70%

Various laboratory equipment was employed in the course of this study to aid sample preparation, analysis, and synthesis. The equipment used is presented in Table 2.

Table 2: Some of the Equipment used for the study

Equipment	Model
Heating mantle	Electrothermal M3847102
Weighing balance	Milton MA203E
Spectrophotometer	DR 9000 HACN
Muffle furnace	Carbonite HTF 1700
Drying oven	LD-201-E-Vision Scientific
Electric blender	CB15P
Electric weighing balance	JJ623BC

Sample Collection Site

The incinerator bottom ash (IBA) used in this study was collected from the Olutee Integrated Waste Management Facility, located in Owain Community, Udu Local Government Area, Delta State, Nigeria. The facility is a major waste management site where municipal solid waste is incinerated, producing bottom ash as one of the by-products. This location was chosen as the source of IBA for the study due to its high volume of municipal waste processing.

Methods

Collection and preparation of samples

Incinerator Bottom Ash (IBA) The IBA sample was collected directly from the Olutee Integrated Waste Management Facility. Collection was carried out using hand gloves, a nose mask, polythene bags, a stainless-steel shovel, a spatula, and a plastic container. The collected ash was sealed, labeled, and transported to the laboratory for subsequent analysis

Plantain peels

Fresh plantain peels were obtained from local food vendors within the Federal University of Petroleum Resources, Effurun, Delta State. The peels were thoroughly washed with distilled water to remove debris and air-dried at room temperature for two weeks. The dried peels were ground using an electric blender, weighed using an electronic balance, and then carbonized in a muffle furnace, with porcelain crucibles serving as holders.

Synthesis of Carbon dots

The synthesis of carbon dots was carried out following the method described by Bibekananda and Niranjan [15]. A total of 500g of dried plantain peels was carbonized in a muffle furnace at 400^{O}C for 2 hours. The obtained carbonized material was allowed to cool, pulverized using a mortar and pestle, and sieved to obtain a fine carbon powder. Subsequently 10g of the powdered carbon was dispersed in 1000 mL distilled water and transferred into a Teflon-lined stainless-steel autoclave for hydrothermal treatment at 400^{O}C for 4 hours. After cooling to room temperature, the suspension was centrifugated at 8,000 revolutions per minute (rpm) for 15 minutes to remove larger particulates. The resulting residue was dried in a hot air oven at 100^{O}C until stable powder was obtained (Plate 1 and 2). The synthesized carbon dot was then characterized by instrumental analysis like the UV-Visible spectrophotometry, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction and Brunauer Emmet Teller Spectroscopy (BET).

Plate 1: Hydrothermal Synthesis of Carbon dot (Source this study)

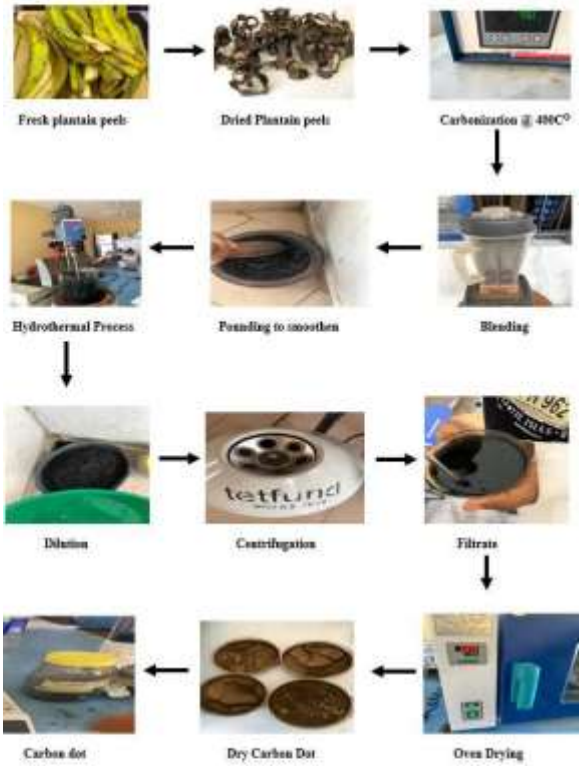

Plate 2: Flow diagram for the synthesis of carbon dot (Source: This study)

Determination of heavy metals in (IBA) and treated samples

To determine the concentration of heavy metals in the incinerator bottom ash (IBA), digestion was first carried out on the untreated sample. One (1g) of IBA was weighed and transferred into a Teflon crucible. A mixture of 1 mL hydrofluoric acid (HF), 1 mL perchloric acid ($HClO_4$), and 3 mL nitric acid (HNO_3) was then added. The crucible was heated on a digestion mantle at 150°C until clear fumes were observed. After cooling, deionized water was added to rinse the remaining solution, which was subsequently filtered and stored in clean sample bottles until required for analysis. The same digestion procedure was applied to the treated (IBA) samples prior to heavy metal analysis

Treatment of Incinerator bottom ash (IBA)

The treatment of incinerator bottom ash (IBA) with carbon dot nanoparticles (CDs) was conducted to determine the removal efficiency of selected heavy metals. For each

Four heavy metals—Iron (Fe), Cadmium (Cd), Copper (Cu), and Zinc (Zn)—were selected for treatment because they are commonly found in waste materials and these metals pose significant environmental and health risks due to their ability to bio magnify across food chain. For each experimental run, 1g of IBA was mixed with 1g of CDs in 98 mL of distilled water. The suspension was stirred thoroughly to ensure uniform dispersion of the nanoparticles. The mixture was then allowed to stand for predetermined contact times of 30 seconds, 2 hours, 4 hours, 6 hours, 8 hours, and 24 hours. At the end of each interval, the samples were centrifuged at 8,000 rpm to separate the carbon dots from the ash residue.

The experimental design and sample preparation are summarized in Table 3

Table 3: Summary of Experimental Design for Treatment of IBA with Carbon Dot Nanoparticles

Metal	Contact Times minutes (m)	Number of Experiments per Metal	Replicates	Total Samples
Iron (Fe)	0.53m, 120m, 240m, 360m, 480m, & 1440m	6	3	18
Cadmium (Cd)	0.5m, 120m, 240m, 360m, 480m, & 1440m	6	3	18
Copper (Cu)	0.5m, 120m, 240m, 360m, 480m, & 1440m	6	3	18
Zinc (Zn)	5m, 120m, 240m, 360m, 480m, & 1440m	6	3	18

Total number of treated samples = 72

Following treatment, the residual concentrations of Fe, Cd, Cu, and Zn in the IBA were determined using Atomic Absorption Spectrophotometry (AAS).

Quality Control and Quality Assurance

Control Reference Standard

To verify that the observed removal of heavy metals from incinerator bottom ash was attributable to the carbon dot nanoparticles and not to distilled water alone, a quality control reference standard of copper was prepared. A stock solution of copper (100 mg/L) was first prepared. From this stock, a 10 mg/L solution was obtained by pipetting 10 mL into a 100 mL volumetric flask and diluting to the mark with distilled water. Subsequently, a 2 mg/L working solution was prepared from the 10 mg/L intermediate solution by serial dilution. Precisely, 20 mL of the 10 mg/L solution was transferred into a 100 mL volumetric flask and diluted to the mark with distilled water to yield the 2 mg/L reference standard. One gram of carbon dot nanoparticles was then introduced into the 2 mg/L copper working solution. The mixture was stirred thoroughly and covered, allowing it to stand for 8 hours (1440 minutes).

Adsorption Studies

Adsorption studies were carried out to evaluate the mechanism and efficiency of heavy metal removal from incinerator bottom ash (IBA) using the synthesized carbon dot nanoparticles (CDs). A fixed dose of 1.g of CDs was introduced into 98 mL of distilled water containing a known quantity of IBA. The suspension was continuously stirred to ensure proper contact between the adsorbent and adsorbate. Aliquots of the mixture were collected at predetermined contact times of 0.53 minutes, 120 minutes, 240 minutes, 360 minutes 480 minutes and 1440 minutes. At each interval, the samples were subjected to centrifugation at 8,000 rpm to achieve efficient separation of the carbon dots from the IBA matrix. The treated ash was then analyzed using Atomic Absorption Spectrophotometry (AAS) to determine the residual concentrations of Fe, Zn, Cu, and Cd.

Adsorption of The Heavy Metals unto The Synthesized Carbon Dot

The nature of adsorption was established by fitting adsorption data obtained into three adsorption isotherm models.

Langmuir Isotherm Model

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \text{ ……………………Eqn 1}$$

Freundlich Isotherm Model

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \text{ ………….. Eqn 2}$$

Kinetic Studies

The adsorption kinetics of heavy metals onto carbon dot nanoparticles (CDs) were evaluated using the pseudo-second-order kinetic model. This model was chosen to determine the rate of adsorption and to provide insight into the mechanism of metal uptake, specifically whether chemisorption or physisorption governs the process.

The pseudo-second-order model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 Q_{max}^2} + \frac{t}{Q_{max}} \text{ ....Eqn 3}$$

Comparison with NUPRC Permissible limit for Heavy metals

To evaluate the effectiveness of carbon dot nanoparticles (CDs) in remediating heavy metals from incinerator bottom ash (IBA), the residual concentrations of Iron (Fe), Cadmium (Cd), Copper (Cu), and Zinc (Zn) in the treated samples were compared with the permissible limits established by the Nigerian Upstream Petroleum Regulatory Commission (NUPRC). This comparison allowed for: Assessment of compliance – determining whether the concentrations of heavy metals in the treated IBA meet regulatory requirements for safe disposal or discharge. Evaluation of treatment efficiency – measuring how effectively the CDs reduced the concentrations of metals relative to the regulatory standards.

The treated IBA samples at various contact times were analyzed using Atomic Absorption Spectrophotometry (AAS), and the resulting metal concentrations were directly compared to the NUPRC limits. This step provided a quantitative measure of the remediation performance of the synthesized carbon dot nanoparticles.

III. RESULTS AND DISCUSSION

This section presents the findings of the study and is organized into two main parts:

- Characterization of the Synthesized Carbon Dots (CDs): Analyses confirming the successful formation of the nanoparticles and the evaluation of their physicochemical properties.
- Adsorption Performance of the Carbon Dots in Treating Incinerator Bottom Ash (IBA): This includes kinetic studies, adsorption isotherms, and comparison of the treated ash with permissible regulatory standards

Characterization of the Synthesized Carbon Dots
Characterization of the carbon dots was carried out to confirm their successful formation and to assess structural and surface features that influence their adsorption ability. Techniques employed include UV– Visible spectroscopy (UV-Vis), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) Transition Electron Microscopy (TEM), Fourier Transform Infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET). The results are presented below

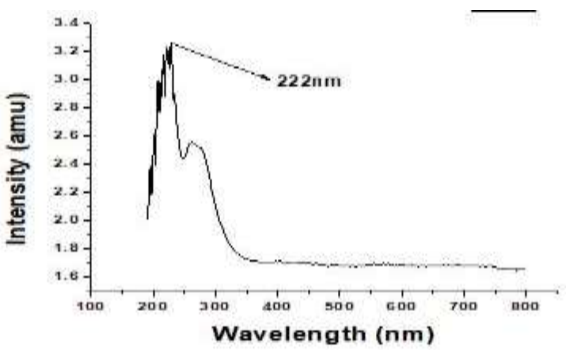

Figure 1: UV- Visible spectra of the synthesized carbon dot

(a) The UV–Visible spectrum of the synthesized carbon dots (Figure 1) exhibited a strong absorption band at approximately 222 nm, located in the deep UV region. This band is attributed to π–π* electronic transitions of aromatic C=C bonds. Although such transitions are more commonly reported in the 260–280 nm range for carbon dots, the observed blue-shift in this study may be linked to several factors, including differences in precursor composition, small particle size (quantum confinement), and the influence of oxygen-containing surface functional groups [19]. The presence of these transitions confirms the existence of conjugated aromatic domains and surface functionalities such as carbonyl and hydroxyl groups. These structural features are important for adsorption, as they provide active binding sites and enhance electronic interactions with heavy metal ions. This optical property is consistent with previous findings on biomass-derived carbon dots, which generally display strong UV absorptions related to π–π* transitions, thereby validating the successful synthesis of functional carbon nanostructures suitable for adsorption processes.

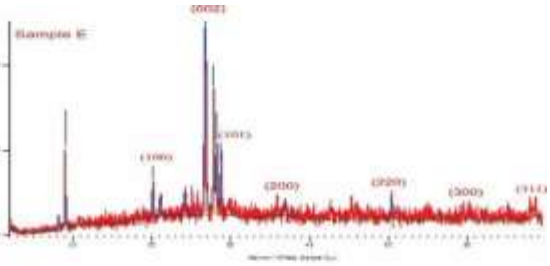

Figure 2: X-ray diffraction spectra of the synthesized carbon dot

(b) The X-ray diffraction (XRD) pattern of the synthesized carbon dots is shown in (Figure 2). A broad diffraction peak was observed at approximately 2θ = 22–24°, which corresponds to the (002) plane of graphitic carbon. The broad and low-intensity nature of this reflection indicates that the carbon dots are predominantly amorphous in structure with low crystallinity, a feature commonly reported for biomass-derived carbon dots. In addition to this broad feature, several small but distinct peaks were observed at lattice planes indexed as (100), (101), (200), (220), (300), and (322). These minor reflections suggest the presence of partially ordered graphitic domains within the otherwise amorphous carbon framework. Such residual crystalline features are often attributed to localized graphitization that occurs during the carbonization process. The coexistence of a broad amorphous peak with weak crystalline reflections indicates that the synthesized carbon dots possess a turbotrain structure a disordered arrangement of sp^2 carbon layers interspersed with short-range ordered graphitic regions. This structural hybrid is advantageous for adsorption processes, as the amorphous domains contribute high surface area and abundant functional groups, while the partially crystalline regions enhance structural stability and electron transfer properties. These observations are in agreement with previous reports on biomass-derived carbon dots, where a broad amorphous (002) peak accompanied by weak crystalline reflections was used to confirm the coexistence of disordered and partially graphitic domains [28].

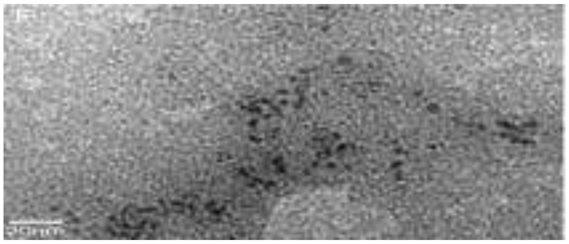

Figure 3: SEM Spectra of the synthesized carbon-dot

(c) The surface morphology of the synthesized carbon dots was examined using Scanning Electron Microscopy (SEM), as shown in (Figure 3). The micrographs revealed that the nanoparticles predominantly exhibited a spherical morphology, which is characteristic of carbon dots synthesized from biomass precursors. The particles appeared relatively uniform in shape, confirming the successful synthesis of nanostructures with consistent morphology. In addition, the SEM images suggested that the carbon dots were well-dispersed, with only minor tendencies toward aggregation, a feature that is expected due to the presence of surface functional groups capable of hydrogen bonding and electrostatic interactions. The relatively small particle sizes and spherical geometry provide a large surface-to-volume ratio, which is an important factor that enhances the adsorption efficiency of carbon dots in removing heavy metals from aqueous media. These morphological characteristics, predominantly spherical particles with slight aggregation, are consistent with earlier reports on carbon dots synthesized from agricultural waste materials, where SEM analyses similarly revealed uniform nanoscale structures with good dispersion. Such agreement with literature further validates the successful formation of carbon dots in this study [20].

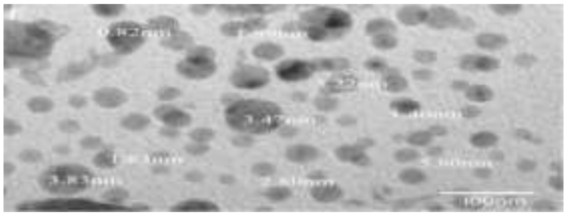

Figure 4: TEM Spectra of the synthesized carbon-dot.

(d) To further investigate the structural features of the synthesized carbon dots, Transmission Electron Microscopy (TEM) was performed, as shown in (Figure 4). The TEM images revealed predominantly spherical nanoparticles with good dispersion and minimal aggregation, indicating stable colloidal behavior. The sizes of the carbon dot obtained was plotted against frequency Figure 5.

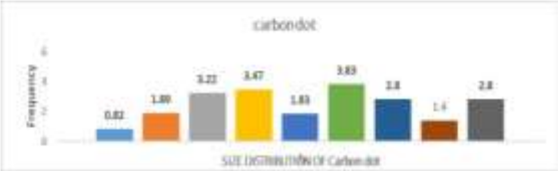

Figure: 5: TEM size distribution of the synthesized carbon dot

The particle sizes measured from the TEM images (Figure 5) ranges from 0.82 nm to 3.83 nm, with many particles around 2–3 nm, giving an average size of approximately 2.78 nm. The variation in particle sizes is expected in biomass-derived carbon dots due to the inherent heterogeneity of the precursor material and the synthesis process. The small particle size and well-dispersed nature of the carbon dots are particularly important for adsorption applications, as they provide a high surface-to-volume ratio and abundant surface functional groups, both of which enhance the interaction with heavy metal ions in aqueous media. These TEM observations are consistent with earlier studies on biomass-derived carbon dots, where spherical nanoparticles in the 1–5 nm range with good dispersion were commonly reported [25].

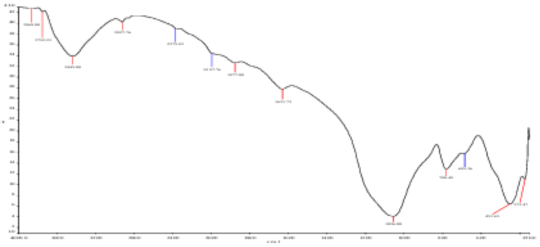

Figure 6: FTIR Spectrum of the carbon dot from plantain peels

(e) The FTIR spectrum of the synthesized carbon dots from plantain peels is shown in (Figure 6). Several distinct absorption bands were observed, indicating the presence of oxygen- and nitrogen-containing functional groups on the nanoparticle surface. The broad band at 3445 cm^{-1} corresponds to O–H stretching vibrations, suggesting abundant hydroxyl groups, while the band at 2927 cm^{-1} corresponds to C–H stretching vibrations. The presence of a peak at 2250 cm^{-1} indicates C≡N stretching, implying nitrogen-containing surface functionalities. Peaks at 1631 cm^{-1} (C=O stretching), 1391 cm^{-1} (C=C stretching), 1122 cm^{-1} (C–O stretching), and 675 cm^{-1} (C–H bending) further confirm the presence of carbonyl, aromatic, alcohol/ether, and aliphatic groups, respectively. The functional groups identified suggest that the carbon dots possess a high density of surface defects and active sites, which are crucial for adsorption of heavy metal ions. Hydroxyl, carbonyl, and nitrile groups can interact with metals through coordination bonding or electrostatic interactions, enhancing the removal efficiency of Iron, Cadmium, Copper, and Zinc from the incinerator bottom ash. Compared to previous reports, these results are consistent with biomass-derived carbon dots, which also display rich surface functionalities that improve adsorption and chemical reactivity [25]. Notably, the combination of oxygen- and nitrogen-containing groups in this study may provide synergistic adsorption sites, making the synthesized carbon dots particularly effective for heavy metal removal.

(f) Brunauer−Emmett−Teller (BET) Surface Area Analysis:

Table 4: Surface area, pore volume and pore average diameter from BET

Material	Functionalized Carbon dot
Surface area (m^2/g)	999.900
Total pore volume (cm^3/g)	0.15540
The pore’s average diameter (nm)	3.005

The BET analysis of the synthesized carbon dots revealed a very high specific surface area of 999.900 m^2/g, a total pore volume of 0.15540 cm^3/g, and an average pore diameter of 3.005 nm (Table 4.). The high surface area indicates that the carbon dots provide a large number of accessible adsorption sites, which is critical for binding heavy metal ions. The measured pore diameter falls within the mesoporous range (2−50 nm), suggesting that the nanoparticles possess pores large enough to facilitate diffusion of metal ions into the interior of the carbon dots. The combination of microporosity high surface area, and surface functional groups enhances the interaction between the carbon dots and metal ions, which is expected to improve the removal efficiency of Iron, Cadmium, Copper, and Zinc from incinerator bottom ash. These findings demonstrate that the synthesized carbon dots are structurally suited for adsorption-based environmental remediation applications, as both surface area and porosity are key parameters governing adsorption capacity and kinetics [30].

Heavy Metals in Raw IBA Before Treatment with carbon dot.

The mean concentrations of heavy metals in the IBA before treatment are presented in (Table 5) and (Figure 7)

Table 5: Mean concentrations of heavy metal in raw IBA before treatment with carbon dot

Parameters	mg/kg
Iron	29.141± 3.0
Cadmium	1561± 45.0
Copper	0.456± 0.02
Zinc	1181± 38.0

Cadmium (Cd) and zinc (Zn) were present at substantially higher concentrations (1561 ± 45.0 mg/kg and 1181 ± 38.0 mg/kg, respectively) compared to iron (Fe, 29.141 ± 3.0 mg/kg) and copper (Cu, 0.456 ± 0.02 mg/kg). The elevated levels of Cd and Zn indicate a significant contamination risk, as both metals are known to be toxic even at relatively low concentrations and can accumulate in soil and aquatic ecosystems. Their presence at these concentrations suggests that the incinerator ash likely contains a mixture of industrial and municipal waste, including electronic components, batteries, and metallic residues. In contrast, the lower concentrations of iron (Fe) and copper (Cu) may reflect the comparatively limited input of these metals from the waste stream. The variation in metal concentrations, as indicated by the standard deviations, reflects the heterogeneous nature of incinerator bottom ash, which is expected given the diverse composition of waste materials. Such variability can influence the efficiency of remediation strategies and underscores the necessity for an adsorbent with high surface area and multifunctional binding sites, such as the synthesized carbon dots used in this study.

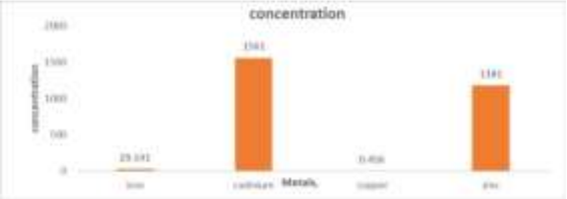

Figure 7: Mean concentrations of heavy metals in (IBA) before treatment with carbon dot.

Heavy metals in the treated incinerator bottom ash (IBA) after contact with carbon dot

The mean results obtained for iron (Fe), cadmium (Cd) copper (Cu) and zinc (Zn) in the treated samples are presented in Table 6 to 9 respectively. The mean concentrations of iron (Fe) in incinerator bottom ash (IBA) after treatment with carbon dot nanoparticles at different contact times are presented in Table 6.

Table 6: Mean concentration of Iron (Fe) in incinerator bottom ash (IBA) sample after treatment with carbon dot

TIME minutes	Fe (mg/kg)	Percentage Efficiency
0.53m	28.12±3.0	3.50
120m	5.091±0.12	82.53
240m	4.082±0.11	85.99
360m	3.045±0.09	89.55
480m	0.001±0.001	99.99
1440m	5.855±0.14	79.90

The removal efficiency of iron (Fe) increased rapidly with time, indicating that adsorption by the carbon dots is time-dependent. At 0.53 minutes, the iron (Fe) concentration was 28.12 ± 3.0 mg/kg, corresponding to a negligible removal efficiency of 3.50%. This low initial removal suggests that adsorption had just begun, with limited interaction between Fe ions and the active sites on the carbon dots. As the contact time increased to 120 minutes, 240minutes, and 360 minutes, the Fe concentrations decreased progressively to 5.091 ± 0.12 mg/kg, 4.082 ± 0.11 mg/kg, and 3.045 ± 0.09 mg/kg, respectively, corresponding to removal efficiencies of 82.53%, 85.99%, and 89.55%. This trend demonstrates that longer contact times allow more Fe ions to diffuse to and bind with the functional groups on the carbon dot surfaces, consistent with typical adsorption kinetics. After 480 minutes, the Fe concentration reached a minimum of 0.001 ± 0.001 mg/kg, achieving a maximum removal efficiency of 99.99%. This indicates that the carbon dots possess a high affinity for Fe ions, and the majority of adsorption occurs within this time frame. Interestingly, at 1440minutes, the Fe concentration slightly increased to 5.855 ± 0.14 mg/kg, reducing the removal efficiency to 79.90%. This suggests that desorption or release of Fe from the carbon dot surfaces may have occurred, possibly due to saturation effects or changes in equilibrium conditions over extended contact times. The mean concentrations of cadmium (Cd) in incinerator bottom ash (IBA) after treatment with carbon dot nanoparticles are presented in Table 7.

Table 7: Mean concentrations of cadmium (Cd) in incinerator bottom ash (IBA) sample after treatment with carbon dot nanoparticles.

TIME	Cadmium (Cd)	Percentage Efficiency
0.53m	1541 ± 0.05	1.28
120m	53.6±0.52	96.56
240m	1.84± 0.01	99.88
360m	0.063±0.002	99.97
480m	<0.001	99.99
1440m	<0.001	99.99

The removal efficiency of Cadmium (Cd) increased sharply with contact time, demonstrating the high affinity of carbon dots for Cd ions. At 0.53 minutes, the Cd concentration was 1541 ± 0.05 mg/kg, corresponding to a minimal removal efficiency of 1.28%, indicating that adsorption had just begun (Table 7). After 120 minutes, the Cd concentration dropped significantly to 53.6 ± 0.52 mg/kg, achieving 96.56% removal. This rapid decrease demonstrates that the carbon dots provide abundant active sites that quickly interact with Cd ions. Further increase in contact time to 240 and 360 minutes reduced the Cd concentration to 1.84 ± 0.01 mg/kg and 0.063 ± 0.002 mg/kg, corresponding to 99.88% and 99.97% removal, respectively. At 480 minutes and 1440 minutes, the Cd concentration was below the detection limit (<0.001 mg/kg), achieving a maximum removal efficiency of 99.99%. The results indicate that the majority of cadmium removal occurs within the first 6 hours of contact, after which equilibrium is reached and almost complete adsorption is achieved. The extremely high removal efficiency demonstrates that carbon dot nanoparticles are highly effective for Cd remediation, likely due to strong interactions between Cd ions and oxygen- and nitrogen-containing functional groups on the nanoparticle surfaces. The mean concentrations of zinc (Zn) in incinerator bottom ash (IBA) after treatment with carbon dot nanoparticles are presented in Table 8.

Table 8: Mean concentrations of zinc (Zn) in incinerator bottom ash (IBA) after treatment with carbon dot nanoparticles.

TIME Minutes	Zinc (Zn) (mg/kg)	Percentage Efficiency
0.53m	1100±38.0	6.86
120m	1057±32.0	10.50
240m	456.74±11.6	61.3
360m	100.61±9.2	91.4
480m	10.05±0.05	99.15
1440m	500.85±12.5	57.6

The removal efficiency of Zinc (Zn) increased progressively with contact time, showing that the carbon dots have a significant affinity for Zn ions. At 0.53 minutes, the Zn concentration was 1100 ± 38.0 mg/kg, corresponding to a low removal efficiency of 6.86%, indicating that adsorption had just begun (Table 8). By 120 minutes, the Zn concentration decreased slightly to 1057 ± 32.0 mg/kg, resulting in a removal efficiency of 10.50%, showing that a small fraction of Zn ions had interacted with the carbon dot surfaces. A notable decrease in Zn concentration was observed at 240 minutes, where the value dropped to 456.74 ± 11.6 mg/kg, corresponding to 61.3% removal. Further contact time to 360 minutes reduced Zn concentration to 100.61 ± 9.2 mg/kg, achieving 91.4% removal, demonstrating that the majority of adsorption occurs during this period as Zn ions occupy available active sites on the carbon dots. Maximum removal was achieved at 480 minutes, with Zn concentration reaching 10.05 ± 0.05 mg/kg, corresponding to 99.15% removal. This shows that carbon dot nanoparticles are highly effective at capturing Zn ions, likely due to interactions with oxygen- and nitrogen-containing functional groups on their surfaces. Interestingly, at 1440 minutes (24 hours), the Zn concentration increased to 500.85 ± 12.5 mg/kg, reducing the removal efficiency to 57.6%. This suggests that partial desorption of Zn occurred, possibly due to equilibrium shifts or saturation of adsorption sites over extended contact time. The mean concentrations of the copper quality control reference standard after treatment with carbon dot nanoparticles are presented in Table 9.

Table 9: Mean concentration copper after treatment with carbon dot

TIME minutes	Copper (Cu) mg/L	Percentage removal Efficiency
0.53	1.994±0.002	0.3
120	0.914±0.002	54.3
240	0.418±0.002	79.1
360	0.191±0.001	90.5
480	0.087±0.001	95.7
1440	0.994±0.002	50.3

The copper concentration of 2.0 mg/L showed only a slight reduction to 1.994 mg/L after 0.53 minutes, corresponding to a 0.3% removal efficiency (Table 9). This minimal change indicates that the adsorption process was not instantaneous, but required sufficient contact time for effective interaction between copper ions and the active sites of the carbon dots. After 2 hours (120 min), a marked decrease was observed, with copper concentration reduced to 0.914 mg/L, achieving a 54.3% removal efficiency. This sharp decline suggests the onset of rapid adsorption as more binding sites became available for copper ion interaction. By 4 hours (240 min), the concentration further decreased to 0.418 mg/L, corresponding to a 79.1% removal efficiency. This stage likely reflects the transition towards equilibrium, as adsorption sites became progressively saturated. Continued contact led to further reductions: at 6 hours (360 min), copper concentration dropped to 0.191 mg/L (90.5% removal), and at 8 hours (480 min), only 0.087 mg/L remained, corresponding to a 95.7% removal efficiency. These results highlight the high adsorption capacity and strong affinity of the carbon dots for copper ions, particularly within the first 8 hours of treatment. However, after 24 hours (1440 min), the copper concentration increased again to 0.994 mg/L, reducing the efficiency to 50.3%. This reversal suggests possible desorption of copper ions from the carbon dot surface, or the attainment of a dynamic equilibrium in which adsorption and desorption occurred simultaneously. Similar trends have been reported in adsorption studies, where extended contact time led to the release of previously bound ions, likely due to site saturation, structural rearrangements, or competing surface interactions. The concentration of heavy metals after treatment with carbon dot are presented in Figure 6

Figure 8: Mean concentrations of heavy metals in (IBA) after treatment with carbon dot

A remarkable reduction in heavy metal concentrations was observed compared to the initial values (Figure 8). Iron (Fe) decreased from 29.141 mg/kg to 0.001 mg/kg, cadmium (Cd) dropped from 1,561 mg/kg to <0.001 mg/kg, copper (Cu) was lowered to 0.08 mg/L, well below the reference standard of 2 mg/L, and zinc (Zn) declined from 1,181 mg/kg to 10.05 mg/kg, remaining under the permissible limit of 50 mg/kg.

Adsorption Studies

Adsorption Isotherm Studies

The adsorption studies results obtained for iron (Fe), cadmium (Cd), and zinc (Zn) are presented from Figure 9 to 14

A plot of Log qe against Log Ce

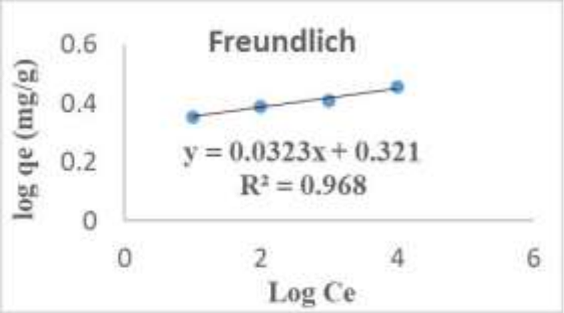

Figure 9: Freundlich adsorption for iron

A plot of Ce/qe Against Ce

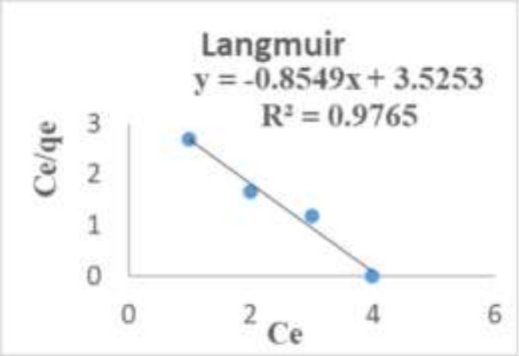

Figure 10: Langmuir adsorption graph for Iron

A plot of Log qe against Log Ce

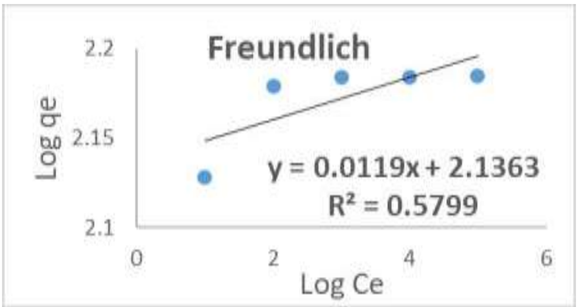

Figure 11: Freundlich adsorption for cadmium

A plot of Ce/qe Against Ce

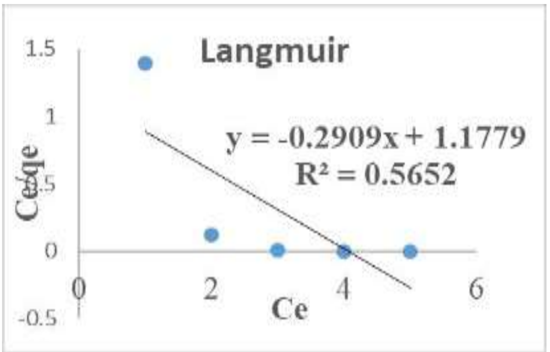

Figure 12: Langmuir adsorption cadmium

A plot of Log qe against Log Ce

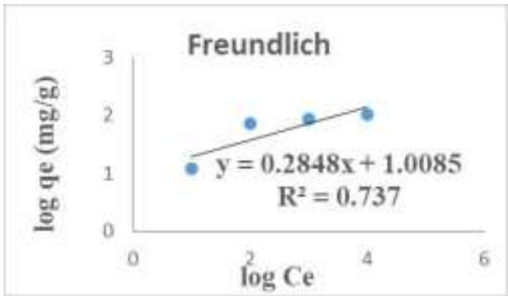

Figure 13: Freundlich adsorption for zinc

A plot of Ce/qe Against Ce

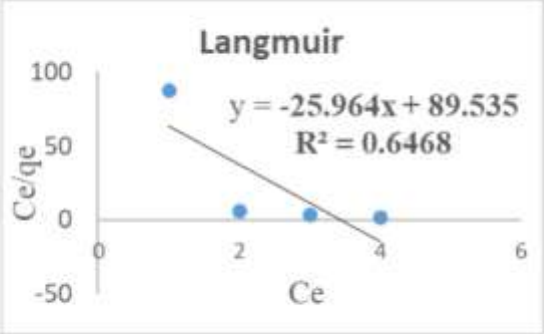

Figure 14: Langmuir adsorption for zinc

The data from the adsorption of heavy metals by carbon dot were fitted into the Freundlich and Langmuir isotherm models to understand the adsorption mechanism of these metals onto the synthesized carbon dots.

For iron (Fe), the Freundlich adsorption plot (Figure 9) produced a positive slope of 0.0323 with a high coefficient of determination ($R^2 = 0.968$). In contrast, the Langmuir adsorption plot (Figure 10) yielded a negative slope of −0.8549, although the coefficient of determination was also high ($R^2 = 0.9765$).

For cadmium (Cd), the Freundlich plot (Figure 11) gave a positive slope of 0.0119 with correlation ($R^2 = 0.5799$). The Langmuir plot (Figure 12) however, showed a negative slope of -0.2909, with coefficient determination of ($R^2 = 0.5652$).

For zinc (Zn), the Freundlich plot (Figure 13) yielded a positive slope of 0.2848 with an (R^2 of 0.737), whereas the Langmuir plot (Figure 14) produced a negative slope of −25,964 with a lower correlation ($R^2 = 0.6468$).

The results clearly show that adsorption of iron (Fe), cadmium (Cd), and zinc (Zn) onto carbon dots is best explained by the Freundlich isotherm. This conclusion is based on the:

- Positive slope values obtained in the Freundlich model.

A positive slope in adsorption isotherm plots indicates that the adsorption constant is valid and meaningful, signifying a feasible adsorption process. On the other hand, a negative slope, as seen in all Langmuir plots in this study, suggests non-physical or invalid adsorption behavior [29]. Negative slopes in adsorption plots imply that the calculated adsorption constants would be negative, which has no practical interpretation in adsorption theory, since adsorption capacity and binding constants must be positive to represent real adsorption. For this reason, Langmuir models with negative slopes are rejected, regardless of how close their R^2 values are to unity.

The Freundlich model describes adsorption on a heterogeneous surface with multiple active sites, leading to multilayer adsorption [21]. This aligns well with the chemical structure of carbon dots, which possess diverse functional groups such as hydroxyl (–OH), carboxyl (–COOH), and amino (–NH) groups. These groups create adsorption sites with varying affinities and energies, enabling strong interactions with Fe, Cd, and Zn ions through ion exchange, complexation, electrostatic attraction, and hydrogen bonding [22].

By contrast, the Langmuir model assumes that adsorption occurs as a monolayer on a homogeneous surface, with all adsorption sites having uniform energy and no interaction between adsorbed molecules [32]. Since the slopes obtained were negative, the Langmuir constants derived would be meaningless, confirming that adsorption in this system does not conform to the monolayer assumption.

Thus, the overall implication of the Freundlich fit is that adsorption of Fe, Cd, and Zn onto carbon dots is a multilayer process on heterogeneous surfaces, which is consistent with the known structural and chemical diversity of carbon-based nanomaterials. Similar observations have been reported by Gupta and Nayak [31]. Who emphasized that the Freundlich model often provides a better description of heavy metal adsorption onto bio-based and carbonaceous adsorbents than the Langmuir model.

Adsorption capacity (q_e) is a key parameter in adsorption studies. It refers to the amount of adsorbate (metal ions) adsorbed per unit mass of adsorbent (carbon dot nanoparticles) at equilibrium. In simple terms, adsorption capacity tells us how much metal can be removed at a given time by the carbon dot. This makes it very important in evaluating the performance of any adsorbent material, since higher adsorption capacities translate to higher removal efficiencies. In this research, adsorption capacity is particularly significant because it provides a direct measure of how effective the synthesized carbon dot nanoparticles are in removing heavy metals from incinerator bottom ash, thereby serving as a benchmark for their potential application in environmental remediation. The Effect of contact time on the adsorption capacities of iron (Fe), cadmium (Cd), and zinc (Zn) onto the synthesized carbon dot nanoparticles are presented in (Figures 15 – 18).

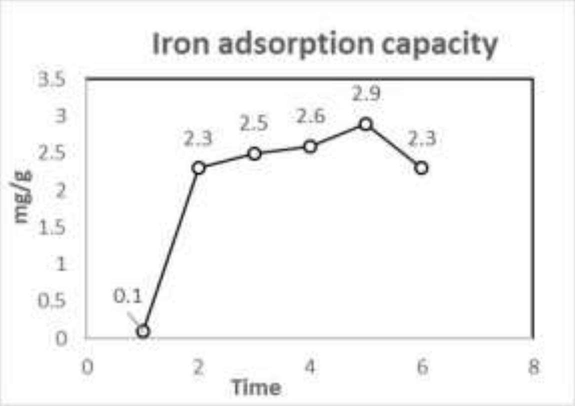

Figure 15: Iron adsorption capacity

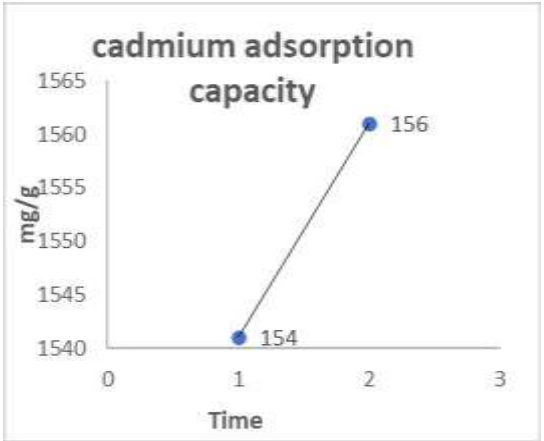

Figure 16: cadmium adsorption capacity

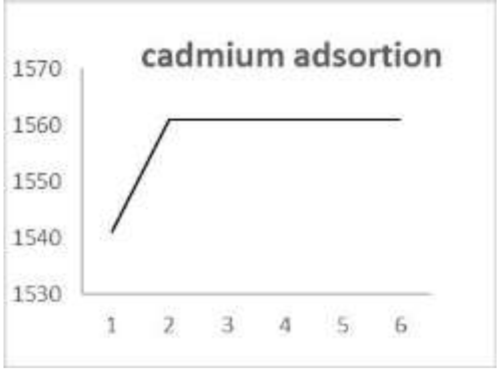

Figure 17: cadmium adsorption capacity

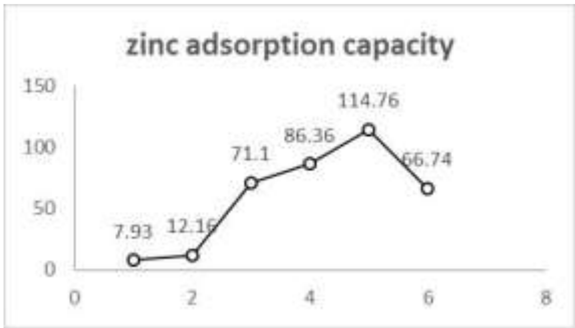

Figure 18: zinc adsorption capacity

As presented in Figure 15, the adsorption of Fe onto the carbon dots increased steadily with time. At 0.53 minutes to 1 hour, the adsorption capacity was only 0.1 mg/g. This value increased to 2.3 mg/g at 120 minutes (2 hours), 2.5 mg/g at 240 minutes (4 hours), and 2.6 mg/g at 360 minutes (6 hours). The maximum adsorption capacity was observed at 480 minutes (8 hours) with 2.9 mg/g, after which a decline occurred, and the adsorption capacity reduced to 2.3 mg/g at 1440 minutes (24 hours). The gradual increase in Fe adsorption suggests a diffusion-controlled process, while the subsequent decline may be attributed to desorption or competition for adsorption sites. A completely different adsorption trend was observed for Cd (Figure 16). At exactly 0.53 minutes (30seconds), the carbon dots exhibited an exceptionally high adsorption capacity of 154 mg/g. This value increased slightly to 156 mg/g at 120 minutes (2 hours) and then remained constant, indicating that almost all Cd ions were rapidly removed within the initial contact period. This implies that for every 0.53 minutes (30 seconds) approximately 154 mg/g of Cd ions are removed from the incinerator bottom ash. Such rapid uptake suggests that Cd ions formed strong chemical bonds with the carbon dots, a process attributed to chemisorption, where functional groups (e.g., carboxylic, hydroxyl, and carbonyl) on the carbon dots interact strongly with (Cd) ions. Further treatment of the IBA did not significantly alter the adsorption pattern because most (Cd) ions had already been removed between 0.53 minutes (30 seconds) to (120 minutes) 2 hours Figure 17 This finding agrees with the result of Kumar *et al*. [29], who reported on the rapid Cd uptake on carbon nanomaterials due to strong coordination with oxygen-containing groups. Likewise, Zhou *et al.* (2019) observed that cadmium (Cd) ions form stable complexes with carboxyl and hydroxyl functional groups, supporting the chemisorption mechanism proposed here. The adsorption pattern of zinc (Zn) (Figure 18) was similar to that of iron (Fe) but with much higher adsorption capacities. At 0.53 minutes to 1 hour, the adsorption capacity was 7.93 mg/g, increasing steadily to 12.16 mg/g at 120 minutes (2 hours), 71.1 mg/g at 240 minutes (4 hours), and 86.36 mg/g. At 360 minutes (6 hours). The maximum adsorption was recorded at 480 minutes (8 hours) with 114.76 mg/g, after which a decline to 66.74 mg/g at 1440 minutes (24 hours) was observed, possibly due to adsorbent site saturation or partial desorption of Zn ions.

The adsorption behaviour was further evaluated using the Freundlich isotherm model, which is expressed as:
$qe = KF\ C_e^{1/n}$
where K_F is the adsorption capacity constant and n is the adsorption intensity constant related to surface heterogeneity. The value of n provides important insight into the nature of adsorption if the value of n is greater than 1 (n>1) the adsorption process is considered favorable, indicating strong affinity between adsorbent (carbon dot) and adsorbate (heavy metals). However, if after adsorption studies the value of n is found to be equal to 1 (n=1) the adsorption is said to be linear, reflecting simple partitioning between phases without specific site preference and when the value of n is less than 1 (i.e. n<1) the adsorption process is unfavorable, suggesting weak interactions or non-ideal adsorption.

In this study, the Freundlich constant, n was greater than 1 for all Freundlich plot confirming that the adsorption of iron (Fe), cadmium (Cd), and zinc (Zn) onto the carbon dots was favorable. This finding is consistent with the BET characterization, which revealed a very high surface area (999.900 m^2/g), an average pore diameter of 3.005 nm, and a total pore volume of 0.15540 cm^3/g. The pore size falls within the mesoporous range (2−50 nm), which facilitates ion diffusion and explains the gradual uptake of Fe and Zn through a diffusion-controlled mechanism. In contrast, the rapid and almost instantaneous removal of Cd is better explained by chemisorption, where the oxygen-containing functional groups on the carbon dots formed strong coordination bonds with Cd ions. Thus, the BET structural features not only provided abundant and accessible adsorption sites but also supported the dual adsorption mechanisms observed: diffusion-controlled physisorption for Fe and Zn, and chemisorption for Cd. Chemisorption (chemical adsorption) occurs when adsorbate molecules or ions form strong chemical bonds (such as covalent, ionic, or coordination bonds) with active sites on the adsorbent surface. Unlike physisorption, which relies on weak van der Waals forces and is usually reversible, chemisorption involves high binding energies (typically 40−800 kJ/mol), site specificity, and often irreversibility. Once formed, these bonds are stable, and the adsorbate may alter the electronic structure of the adsorbent surface.

In this reaction system, the oxygen-containing functional groups on the carbon dots (−COOH, −OH, −C=O) acted as electron donors that coordinated with Cd^{2+} ions, leading to the formation of strong surface complexes. This explains why Cd was removed almost completely within the first few minutes and why further treatment did not significantly change the adsorption pattern.

Kinetic Studies

Kinetic studies are essential in adsorption research because they help to reveal the mechanism and rate at which heavy metals are adsorbed onto an adsorbent surface. In this study, the adsorption of Fe, Cd, and Zn onto the synthesized carbon dots was modeled using the Pseudo-second order kinetic model. This model was chosen because it is widely applied to adsorption systems where chemical interactions, such as electron sharing or exchange, are likely to dominate the process [17]. The results of the pseudo-second order kinetic studies are presented in Figures 19−.21

A Plot of t/qt versus time

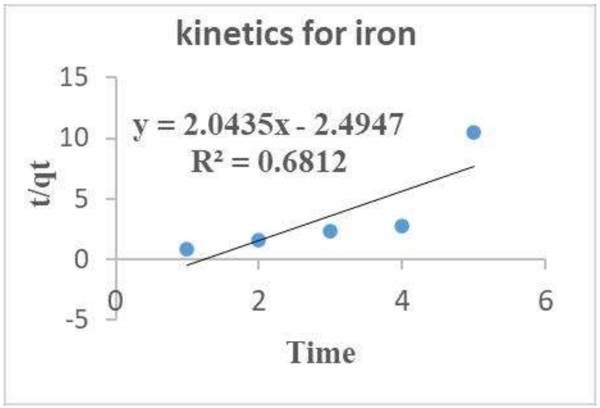

Figure 19: Second order kinetics for Iron

A Plot of t/qt versus time

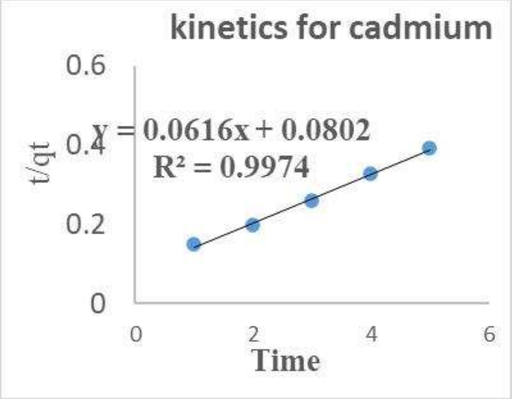

Figure 20: Second order kinetics for cadmium

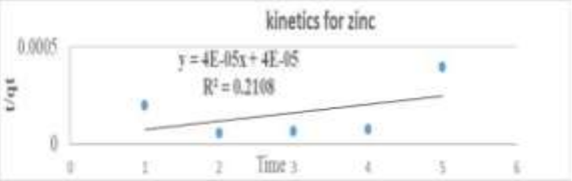

Figure 21: Second order kinetics for zinc

The main criteria for assessing the suitability of the model is the coefficient of determination (R^2). A higher R^2 value, particularly values close to 1.0, indicates that the pseudo-second order kinetic model is able to adequately describe the adsorption process. The kinetic plot for Iron (Figure 19) produced an R^2 value of 0.6812. This relatively low value indicates that the pseudo-second order model does not adequately account for the adsorption behavior of iron unto the carbon dots. The poor fit suggests that the adsorption of iron may be governed by weak physical forces (physisorption), such as Van der Waals interactions, rather than strong chemical bonding. The kinetic plot for cadmium (Figure 20) gave an R^2 value of 0.9974. This excellent fit suggests that the pseudo-second order kinetic model very well describes the adsorption behavior of Cd onto the carbon dots. Since this model is strongly associated with chemisorption mechanisms where adsorption involves valence forces through electron sharing, ion exchange, or covalent bonding it implies that cadmium interacted strongly with the functional groups on the carbon dots. The oxygen- and nitrogen-based groups (−OH, −COOH, − NH_2) likely provided strong binding sites for Cadmium [22]. The kinetic plot for zinc (Figure 21) gave an R^2 value of 0.2108, which is very low. This indicates that the pseudo-second order model poorly explains the adsorption of Zn onto the carbon dots. The weak correlation suggests that zinc adsorption was likely dominated by physisorption mechanisms, with little evidence of strong chemical interaction. The R^2 values serve as the primary basis for determining whether the pseudo-second order model is appropriate for describing adsorption kinetics in this study. A high R^2 (close to 1) indicates chemisorption dominance, while low R^2 values imply that the adsorption is likely governed by weaker physical forces.

Comparison With NUPRC Permissible Limit for heavy Metals

The concentrations of selected heavy metals in incinerator bottom ash (IBA) before and after treatment with carbon dot nanoparticles were compared with the Nigerian Upstream Petroleum Regulatory Commission (NUPRC) permissible limits for safe disposal into the environment. The results are presented in Table 10.

Table 10: Heavy Metal Concentrations in IBA Compared with NUPRC Permissible Limit

Parameters	IBA Before Treatment	IBA After Treatment	NUPRC
Iron	29.141mg/kg	0.001mg/kg	N/A
Cadmium	1,561 mg/kg	<0.001mg/kg	1.00 mg/kg
Copper	2 mg/L	0.087mg/L	1.00mg/kg
Zinc	1,181 mg/kg	10.05mg/kg	50 mg/kg

The concentration of cadmium (Cd) in untreated IBA was 1,561 mg/kg, exceeding the NUPRC permissible limit of 1.00 mg/kg by more than 1,500-fold. Such extreme levels represent a major environmental and health hazard, as Cd is highly toxic, persistent, and capable of bioaccumulating in crops, aquatic organisms, and ultimately the human food chain. Following treatment with carbon dots, the Cd concentration was drastically reduced to <0.001 mg/kg, well below the regulatory threshold. This exceptional removal efficiency is attributed to chemisorption, in which Cd^{2+} ions formed strong coordination bonds with oxygen-containing functional groups (−OH, −COOH, −C=O) present on the surface of the carbon dots, leading to rapid and essentially irreversible uptake.

Similarly, the prepared copper solution used as a quality control reference standard initially contained 2.0 mg/L of Cu, which was above the NUPRC limit of 1.00 mg/kg. After treatment, the concentration decreased significantly to 0.087 mg/L, falling within the safe range. The reduction demonstrates the efficiency of carbon dots in copper remediation, most likely through physisorption and surface complexation, whereby Cu^{2+} ions were adsorbed onto the mesoporous surfaces and active sites of the nanomaterial. Zinc concentration in untreated ash was 1,181 mg/kg, significantly exceeding the NUPRC limit of 50 mg/kg. After treatment, the concentration dropped to 10.05 mg/kg, which is well below the standard. The gradual uptake of Zn, consistent with the adsorption kinetics earlier reported, reflects a diffusion-controlled physisorption process facilitated by the high surface area (999.900 m^2/g) and mesoporous structure (3.005 nm pore diameter) of the carbon dots.

Although no NUPRC limit exists for Fe, the concentration in untreated ash (29.141 mg/kg) was considerably reduced to 0.001 mg/kg after treatment. While Fe is less toxic than Cd, Cu, and Zn, elevated concentrations in the environment can stain water, disrupt aquatic habitats, and alter soil chemistry. Its reduction therefore contributes to the overall safety of treated IBA.

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CONCLUSION

This research demonstrated the successful synthesis of carbon dots from plantain peels using an eco-friendly hydrothermal method. Characterization confirmed that the carbon dots possessed nanoscale dimensions, a porous surface enriched with functional groups, and a partly crystalline structure, all of which enhanced their adsorption potential. When applied to incinerator bottom ash, the carbon dots effectively removed cadmium, iron, copper, and zinc, with removal efficiencies exceeding 90% for all the metals studied. The adsorption of Fe and Zn increased gradually with time, while Cd displayed a much faster uptake, achieving equilibrium within two hours, reflecting different underlying mechanisms. The adsorption behavior was best described by the Freundlich isotherm model, suggesting multilayer adsorption on a heterogeneous surface. Furthermore, the kinetic analysis revealed that cadmium adsorption followed a pseudo-second-order model with a high coefficient of determination ($R^2 = 0.9802$), strongly indicating chemisorption through interaction with the functional groups on the carbon dots. Overall, the findings confirm that carbon dots derived from plantain peels offer a simple, cost-effective, and environmentally friendly approach for the remediation of heavy metals from incinerator bottom ash.

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