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Comparative analysis of activated banana peel variants for biosorption of copper and lead from aqueous solutions

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Abstract

This study investigates the use of banana peel (BP), an abundant agricultural waste, as a low-cost and sustainable biosorbent for the removal of heavy metal ions of Cu (II) and Pb (II) from industrial effluents. A comparative analysis was conducted on various activated banana peel (BP) sorbents including acid-activated, alkali-activated, thermally activated, and chemically-thermally activated forms to evaluate and enhance their adsorption performance for copper (Cu^{2+}) and lead (Pb^{2+}) ions. The banana peel sorbents were characterized using Fourier Transform Infrared Spectroscopy (FT-IR) to identify surface functional groups, X-ray Diffraction (XRD) for structural analysis, while Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analyses were employed to examine its morphology and elemental composition. The research evaluates how these activation techniques influence the physicochemical properties and sorptive capacity of the material. The effects of individual parameters such as temperature, contact time, acid/alkali concentration, and pH were thoroughly investigated to determine the optimal conditions and the most effective form of activated banana peel for the efficient removal of toxic metal ions. Optimal conditions were observed around 40-50% concentration, 40-50°C, and pH 4-6, confirming banana peel as a promising low-cost biosorbent for heavy metal removal. Amongst all treatments, chemico-thermally activated banana peel exhibited the best adsorption performance, removing up to 88-89% of Pb(II) and 74% of Cu(II) under optimized conditions. Acid and alkali activation improved removal to 70-72% for Pb (II) and 54-84% for Cu (II), compared to only 20-27% for untreated peel. The studies are supported by kinetic and isotherm models. The adsorption of Cu(II) and Pb(II) ions onto chemico-thermally treated activated banana peel was best described by the Freundlich isotherm model ($R^2 = 0.9848$ for Cu(II) and 0.9326 for Pb(II)), indicating multilayer adsorption on a heterogeneous surface. The kinetic analysis revealed that the process predominantly follows a pseudo-second-order model, suggesting chemisorption as the rate-controlling mechanism. The findings provide valuable insights into optimizing BP for practical applications in industrial wastewater treatment, reinforcing its potential as an eco-friendly and effective alternative to conventional adsorbents. Moreover, the comparative analysis enables the identification of the most suitable activation method for achieving optimal adsorption performance.

Keywords: Banana peel, biosorbent, sustainable, eco-friendly

Introduction

In today's world the global Industrial Revolution has resulted in arbitrary discharge of industrial wastewater containing heavy toxic metal ions at an unprecedented rate. The discharge of untreated effluents from industries like leather tanning, electronics, pesticides, paint, thermal power plant, pharmaceuticals, textiles, metal plating and galvanizing, has triggered various health hazards and disturbed ecological equilibrium [1-3]. Some heavy metals that pose major risks due to their toxicity are lead (Pb), chromium (Cr), zinc (Zn), copper (Cu), cadmium (Cd), arsenic (As), nickel (Ni), and mercury (Hg) [4-7]. Although trace levels of heavy metals such as copper and zinc are vital for physiological functions, but their accumulation at high levels can be life threatening. These metals above the threshold limit become carcinogenic and also lead to hyperkeratosis, skin lesions, kidney, stomach, liver and brain problems [8-10].

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A range of methodologies has been employed to remove hazardous compounds from aqueous environment. Some of these experimental techniques include chemical precipitation^[11], membrane separation^[12], reverse osmosis^[13], ion-exchange^[14], coagulation-flocculation^[15], electrodeposition^[16] etc. However, conventional techniques often suffer from drawbacks, like massive consumption of chemicals, high-costs, incomplete removal of trace-level heavy metals and generation of toxic by-products that require further treatment^[17-18]. As a consequence, researchers are more focused of identifying sustainable methods like bio-sorption where a biological material is used as an adsorbent. The mechanism involves interactions between the solid sorbent and the liquid sorbate, and due to high affinity, the sorbent captures unwanted metal species present in the solution^[19]. Bio-sorption is often a promising sustainable biosorbent owing to its low cost, operational simplicity, biodegradability, and eco-friendly nature^[20-21]. A wide variety of natural waste biomass materials such as rice husk, tea and coffee residues, sawdust, orange peels, dried leaves, coconut husk, peanut shells, and tree bark have been reported to possess adsorption capabilities^[22-24]. Banana peel (BP) is a low, environmentally friendly and readily available adsorbent for remediation of a broad spectrum of contaminants. BP's surface is equipped with multiple functional groups, facilitating the sorption of different cationic and anionic species^[25]. Despite significant research on the use of banana peel (BP) for the removal of toxic metals, its full potential remains underutilized, as most research has focused on raw BP rather than its more effective activated forms. Activation of BP is anticipated to enhance the biosorption capacity by increasing the surface area or binding sites of the biosorbent. Studies reveal that pretreatment of BP with nitric acid (HNO₃) resulted in higher Zn biosorption capacity (~2.75 mg/g)^[26].²⁶ This study focuses on the utilization of activated banana peel (BP) for toxic metal ion remediation from industrial wastewater. It presents a comparative analysis of various activation methods applied to BP and their effects on its adsorption potential. By evaluating different activation techniques such as chemical, thermal, or combined treatments; this research aims to identify the most reliable method for augmenting the sorptive capacity of BP toward heavy metal ions. Unlike prior studies that typically focus on a single modification route, this work aims to identify the most effective and reliable method for significantly enhancing BP's capacity to remove heavy metal ions. To the extent of our knowledge, no prior studies have fully explored the influence of different activation approaches on the metal ion removal efficiency of BP. This work, therefore, contributes novel insights into optimizing BP as a low-cost, sustainable, and effective biosorbent for industrial wastewater treatment.

Materials and Methods

Materials: Banana peels were procured from the local market. The banana was from *Musa paradisiaca* L. family as classified according to color index^[27]. Other chemicals like hydrochloric acid (HCl), sodium hydroxide (NaOH), and phosphoric acid (H₃PO₄) used were of analytical grade (AR), purchase from E-Merck. Double distilled water is used in all experiments.

Methods

Synthesis of banana peel biosorbent (BP)

The banana peel was washed thoroughly to clean it from all dirt and impurities. It was then air-dried to remove the

retained moisture content. After few days, the peel was further heated in an oven to remove the remaining moisture at 80°C. The dried peels were pulverized into finer particles using a motor pestle and then washed again. It was then further dried at 50°C for 24 h in an oven, after which the peels were grinded using a blender. The fine powder of BP peel was sieved through the mechanical shaker. This is the raw sample of the BP sorbent.

Stock solutions for both copper and lead are prepared at a 100 ppm (parts per million) of concentration. These stock solutions serve as the primary source for the preparation of more dilute standard solutions. From the 100 ppm stock solutions, standard solutions with a concentration of 5 ppm are prepared. This dilution is achieved by taking 50 mL of the stock solution and diluting it to a final volume of 1000 mL using deionised water. It is important to ensure thorough mixing to achieve a uniform concentration throughout the solution.

The accuracy of these dilutions is critical, as the standard solutions will be used for calibration and analysis.

Synthesis of alkali modified BP biosorbent (aBP)

50 g of prepared BP was taken in conical flasks containing 0.1M NaOH solution. The flask was sealed using aluminium foil to protect it from contamination and left for 2 h. Then the sample was oven-dried at 80°C for 24 h. Finally, the NaOH modified banana peel samples were retrieved after grinding it into powder and sieved from 200 µm sieve sizes.

2.4 Synthesis of thermally modified BP biosorbent (tBP)

The thermally modified BP was produced by carbonizing the raw BP at 450°C for one hour. This condition was selected after testing different temperatures (300, 350, 400, 450, and 500°C) and carbonization durations (30, 60, and 90 minutes). The process was performed in a porcelain crucible using an electric muffle furnace, and the sample was cooled to room temperature afterward to stabilize its properties for the next step.

Synthesis of acid modified BP biosorbent (acBP)

The as-prepared BP powder (50g) was taken in conical flasks containing 0.1 M HCl solution and mixed thoroughly with the help of glass rod. The slurries were subsequently left undisturbed for 2 h to facilitate the activation process. Later, the slurry was washed repeatedly with double distilled DI water to remove any excess acid. The washed samples were left to dry at 80°C for 24 h to acquire the final acid modified BP.

Synthesis of chemically-thermally modified BP biosorbent (ctBP)

This novel BP sorbent was synthesized by treating the BP powder first with H₃PO₄ acid and then after thermally treated at extremely high temperatures. The acid percentage was varied for 10-50% and the temperatures conditions were altered from 300-500°C with the aim to identify the best optimised and suitable parameters for adsorption of both metal ions. The BP after treated with acid and temperature, it was left for further 2 h covered with aluminium foil. Following the treatment, the samples were thoroughly washed with DI water and dried in crucibles at 100°C for 24 h in air oven and stored in desiccators to avoid any contamination or moisture retention.

The optimal characterization parameters in terms of charcoal yield, fixed carbon, ash content, porosity, and

moisture content for acid-activated BP, alkali-activated BP, thermally activated BP, chemically thermally activated BP and inactivated raw BP are given in the Table 1.

Characterization techniques

X-ray diffraction (XRD) measurements were performed at room temperature via Rigaku SmartLab diffractometer featured with Cu K α radiation ($\lambda = 1.542$ nm), over a 2θ range of 10° to 80° . For the analysis, the samples were manually ground into fine powder with a mortar and pestle. Fourier-transform infrared (FTIR) spectroscopy was used to obtain the spectra using a PerkinElmer 3725 spectrometer in the range of 400 to 4000 cm^{-1} . The samples were prepared as KBr pellets by thoroughly mixing a small amount of sample (0.1% w/w relative to KBr) with potassium bromide, grinding the mixture, and pressing it into 7-mm pellets using a die assembly and a manual hydraulic press. The morphology of the samples was examined via LEO 435-VF scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis.

Adsorption Experiments

The adsorption behavior experiments were conducted using a batch methodology. In each trial, of the heavy metal solution was accurately dispensed into a Erlenmeyer flask; the metals Cu (II) and Pb (II) were tested individually to isolate their adsorption characteristics. A constant biosorbent dosage of 2g was introduced into each flask. Specifically, samples of each of the five prepared biosorbents—the inactivated (raw) BP, acid-activated BP, alkali-activated BP, thermally activated BP, and chemically-thermally treated BP—were tested separately against the metal solutions. The resulting mixtures were then incubated, under agitation, for a fixed contact time of 30 mins at room temperature. This controlled incubation period allowed for the sorbent materials to interact with and uptake the metal ions from the solution, enabling the subsequent measurement of their distinct adsorption efficiencies. All adsorption experiments were conducted in batch, and the average results are reported.

The metal ion removal efficiency or the adsorption%, is determined from equation (1) below [28, 29]

$$\text{Removal\%} = (C_i - C_f) / C_i \times 100$$

Where, C_i and C_f are the initial and final concentrations of respective metal ions.

The BP sorbents were studied over a varying pH of 2-7, to expound the influence of pH on adsorption capacity of BPs. For pH adjustments each time sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) solutions were used. The effectiveness of contact time on the adsorption potential of BPs to remove toxic metals was also studied, and contact duration of 30, 60, 90, and 120 min was used. The effect of temperature was also explored and for acid inactivated (BP), activated banana, alkali activated BP temperature span of 20-50°C was used. Whereas, for thermally treated a temperature span of 40-150°C and for chemically-thermally treated BP temperature span of 300-500°C was used. The percentage of acid and alkali was also varied between 10-50% to evaluate the impact of acid/alkali concentration of adsorption ability.

Results

SEM analysis

The structural analysis reveals an irregular and porous surface which is highly desirable for efficient adsorption process. The surface porosity of the biosorbent is necessary for particle diffusion to take place and efficient entrapment of the pollutant in its pores. Similar rough and porous morphology of banana peel sorbent has been observed in literature [30-31]. EDX was also performed to understand the elemental composition of the banana peel as it provides a qualitative and semi-quantitative information about the elemental composition of the sample. The elements present in natural banana peel are as stated in Table 2 below. The high content of carbon and oxygen in banana peels points to their potential as efficient adsorbents. The significant presence of carbon and oxygen suggest a lignocellulosic structure, which is typical of plant-based biomass. The carbon-rich structure provides a large number of active sites and functional groups (such as hydroxyl, carboxyl, and carbonyl), which are crucial for the adsorption of heavy metals, dyes, and other pollutants. Additionally, the presence of mineral elements like K, Ca, and Mg may contribute to ion-exchange mechanisms during adsorption processes.

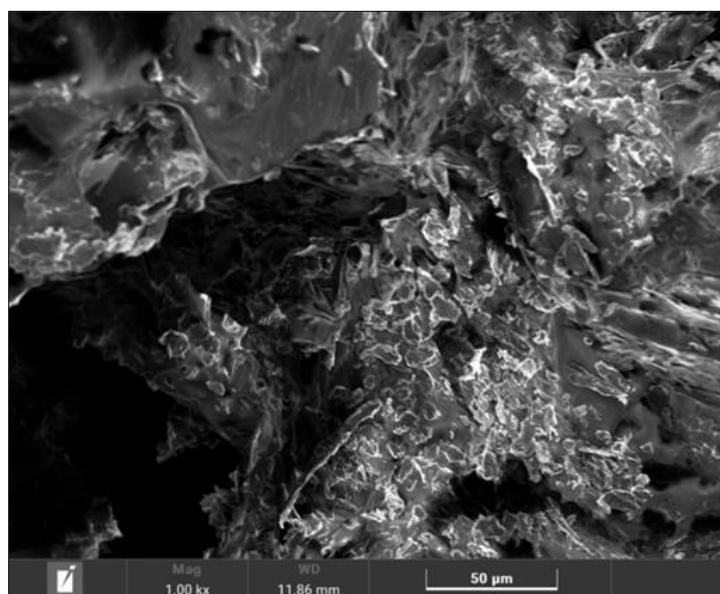


Fig 1: SEM image of the inactivated natural banana peel sorbent

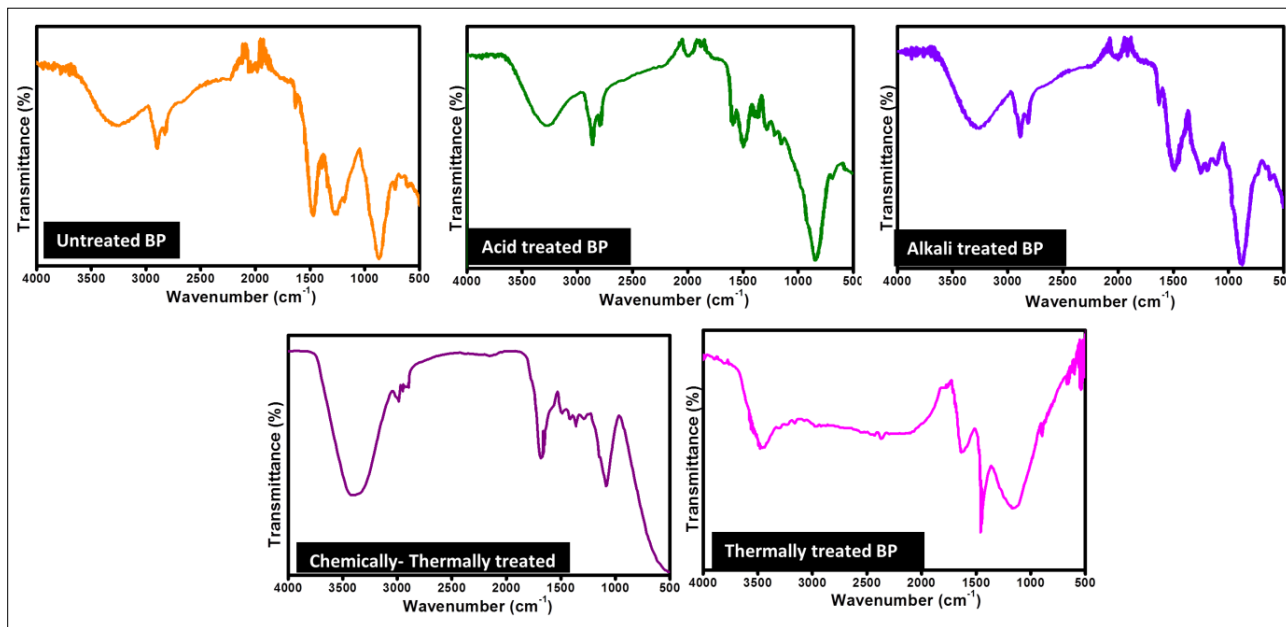
Table 1: EDX analysis of banana peel

Chemical composition (%) of banana peel as obtained in EDX analysis								
C	N	O	Si	K	Na	Mg	P	S
59.71	4.28	34.84	0.11	0.27	0.24	0.07	0.31	0.17

FT-IR Studies

FT-IR was used to analyse the functional groups when raw banana is subjected to activation by different modes. These functional groups offer insights on the porous structure of banana peel and helps in predicting the adsorption properties

of the adsorbent. By analyzing the characteristic absorption frequencies associated with these functional groups, FT-IR provides insights into the molecular structure and chemical environment of the sorbent. Each functional group corresponds to a unique vibrational frequency, which is directly related to the fundamental modes of vibration such as stretching, bending, or twisting of chemical bonds. These vibrational patterns serve as molecular fingerprints, allowing researchers to identify the types of chemical bonds present and any changes they undergo during interactions with impurities.

**Fig 2:** FT-IR analysis in-activated and activated BPs**Table 2:** FT-IR absorption peaks observed in respective BP sorbents

Parameter	Raw BP	Alkali BP	Acid BP	Thermally treated BP	Chemically-thermally treated BP
O-H	3273.25	3269.98	3283.85	3462.48	3380.87
C-H symmetrical	2891.59	2907.39	2868.94	2957.56	2985.41
C-H Asymmetrical	2878.13	2815.55	2783.73	negligent peak	2892.81
C=O	1792.01	1639.14	1782.22	1731.43	1683.47
C-O/C-C	1631.32	1497.86	1586.35	1460.92	1683.47
C-O-H	1255.68	1257.11	1291.32	negligent peak	1360.98
C-O stretching of alkyl	1117.61	1185.6	1149.53	1160.21	1086.59
C-N	883.21	877.23	848.65	888.26	negligent peak

The FT-IR spectra shows presence of O-H, N-H, C-H, C=O, C=C, C-N, C-O and C-H vibrations on the surface conveying that it provides sufficient surface functionality for interaction of toxic metal ions. FTIR analysis as seen in Fig 2 for inactivated and activated BP sorbent indicated the bands that have slightly different values but are around the same range. The observed bands are reported in the table below (Table 2) which are according to the FT-IR studies reported in literature for banana peels [31-33]. As revealed in the structural analysis the banana peel contains a variety of functional groups, including alcohols/phenols, carboxyl, amide, alkane, aromatic, and amine groups. It is widely recognized that in the biomass the hydroxyl, carboxyl groups significantly contribute in the process of adsorption. [34-35]. Carboxylic groups typically exhibit pKa values in the range of 3.8 to 4.8. This means that at pH levels above 4, these groups become deprotonated, acquiring a negative charge that facilitates the electrostatic attraction and binding

of metal ions with positive charge, thereby enhancing the adsorption capacity of the banana peel. Conversely, at pH values below 3, the carboxylic groups remain protonated and neutral, which reduces their ability to bind metal ions due to the lack of electrostatic attraction. This pH-dependent behavior aligns with the experimental observations in this study, where a noticeable increase in adsorption efficiency was recorded at pH levels above 4. The results reinforce the hypothesis that deprotonated carboxyl groups play a crucial role in the metal-binding mechanism, contributing significantly to the overall adsorptive performance of banana peel as a low-cost biosorbent.

XRD analysis

XRD pattern of inactivated raw banana peel sorbent reveals diffraction peaks at 2θ values of approximately 26° and 46° as seen in Fig 3. These peaks correspond to the (002) and (100) planes of carbon-based materials, respectively and

indicate the existence of graphite crystallites within the BP [36]. The diffraction patterns of the activated BPs are not shown here as they presented analogous diffraction peaks with no significant differences in peak positions. The only

noticeable variation was in the sharpness and intensity of the peaks, indicating minor differences in crystallinity among the samples.

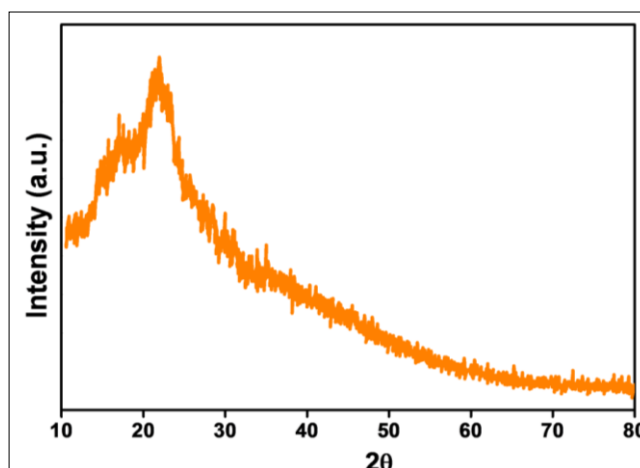


Fig 3: XRD pattern of inactivated raw banana peel sorbent

Effect of Individual Parameters

Effect of pH on removal of Cu (II) ions

In the investigation of pH's effect on the adsorption capability of different types of BP adsorbents, other experimental variables were maintained at a constant value (contact time 120 min, temperature 40°C) and only the pH was varied between 2-7. The data as recorded is tabulated in Table 3. It is noted that at low pH untreated BP, alkali treated BP (aBP), acid treated BP (acBP) and thermally treated BP (tBP) none of the sorbents show Cu (II) ions adsorption. The adsorption was low until 3 pH for these sorbents. As observed in Fig 4a untreated BP shows maximum adsorption at 6, after which adsorption of Cu (II) ions decreases. For aBP maxima is achieved at 5 after which adsorption becomes consistent. For acBP maxima is observed at 4 after which the adsorption decreases rapidly. The tBP sorbent shows maximum adsorption at 5 pH after which it decreases. The tcBP sorbent exhibits a similar adsorption behavior characterized by maximum adsorption efficiency at 5 pH. As the pH increases beyond this optimal acidic range, the adsorption efficiency of all adsorbents gradually declines. This trend suggests that the adsorption

mechanism of BP sorbents is highly sensitive to pH changes, likely due to alterations in the surface charge of the sorbent or the ionization state of the target analytes under varying pH conditions. The results are consistent with the studies reported in literature [37, 38]. The untreated banana peel exhibited the lowest performance, with a maximum removal of only 27.50% at pH 6, highlighting the limited adsorption potential in its raw form. Acid-activated banana peel showed moderate improvement, with the highest Cu(II) removal of 54% at pH 4, indicating that acid treatment can increase active surface sites but still has limited capacity compared to more advanced treatments. In contrast, alkali-activated banana peel demonstrated a significant increase in removal efficiency, particularly from pH 4 to 7, with the highest removal (84.42%) observed at pH 7. Thermally treated banana peel showed only modest performance, with the highest removal (48.12%) occurring at pH 5. While thermal treatment may alter surface structure and porosity, it appears insufficient alone for optimal Cu(II) adsorption. On the other hand, chemico-thermally treated banana peel demonstrated outstanding adsorption capacity, achieving a maximum removal of 88.02% at pH 4.

Table 3: Experimentally recorded values for removal% of Cu (II) and Pb (II) ions of different adsorbents with variation in pH levels

Percentage removal of Cu (II) on activated banana peel (acid) at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%
5	2	3.85	23.00
5	3	3.42	32.00
5	4	2.34	54.00
5	5	2.65	48.00
5	6	2.80	44.00
5	7	3.25	35.00
Percentage removal of Cu (II) on activated banana peel (alkali) at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%
5	2	3.58	28.32
5	3	2.19	56.21
5	4	1.74	65.12
5	5	1.00	80.01
5	6	0.89	82.15
5	7	0.78	84.42
Percentage removal of Cu (II) on activated banana peel (thermally treated) at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%

5	2	4.39	12.25
5	3	3.82	23.54
5	4	2.85	43.02
5	5	2.59	48.12
5	6	2.65	46.98
5	7	2.99	40.21
Percentage removal of Cu (II) on activated banana peel (chemico-thermally treated) at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%
5	2	1.34	73.18
5	3	0.93	81.32
5	4	0.60	88.02
5	5	1.74	65.11
5	6	2.49	50.23
5	7	2.70	46.05
Percentage removal of Cu (II) on untreated banana peel at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%
5	2	4.34	13.21
5	3	4.22	15.55
5	4	4.01	19.76
5	5	3.88	22.40
5	6	3.63	27.50
5	7	3.77	24.70
Percentage removal of Pb (II) on activated banana peel (acid) at various pH			
Initial Conc (ppm)	pH	Final Conc (ppm)	Removal%
5	2	2.89	42.21
5	3	1.83	63.40
5	4	1.08	78.45
5	5	1.64	67.21
5	6	1.94	61.21
5	7	2.80	44.06
Percentage removal of Pb (II) on activated banana peel (alkali) at various pH			
Initial Conc (ppm)	Temperature	Final Conc (ppm)	Removal%
5	2	3.58	28.33
5	3	2.16	56.80
5	4	1.71	65.72
5	5	1.00	80.05
5	6	0.88	82.33
5	7	0.91	81.71
Percentage removal of Pb (II) on activated banana peel (Thermally treated) at			
Initial Conc (ppm)	Temperature	Final Conc (ppm)	Removal%
5	2	3.84	23.21
5	3	3.72	25.53
5	4	2.86	45.00
5	5	2.74	45.21
5	6	3.08	38.45
5	7	3.92	21.80
5	2	1.73	66.08
5	3	0.91	81.88
Percentage removal of Pb (II) on activated banana peel (chemico-thermally treated) at various pH			
Initial Conc (ppm)	Temperature	Final Conc (ppm)	Removal%
5	4	0.62	88.00
5	5	1.75	65.00
5	6	2.51	50.00
5	7	2.72	46.00
Percentage removal of Pb (II) on untreated banana peel (acid) at various pH			
Initial Conc (ppm)	Temperature	Final Conc (ppm)	Removal%
5	2	4.10	18.00
5	3	4.23	20.00
5	4	3.85	23.00
5	5	3.65	27.00
5	6	3.95	21.00
5	7	3.76	25.00

Effect of pH on removal of Pb (II) ions

Similar results were observed for adsorption of Pb (II) ion by different BP sorbents where at lower pH levels not much efficiency in removal of ions is observed. As illustrated in Fig 4b, the untreated BP sorbent exhibits maximum Pb (II)

ion adsorption at pH 5, beyond which the adsorption efficiency begins to decline. For the aBP sorbent, peak adsorption is observed at pH 5, after which the removal efficiency remains relatively stable. On contrary, the acBP sorbent achieves its highest adsorption efficiency at pH 4,

followed by a significant drop in performance at higher pH levels. The tBP sorbent also demonstrates an optimal adsorption capacity at pH 4, beyond which a sudden decline is observed. Similarly, the tcBP sorbent displays its highest adsorption efficiency at pH 4. As the pH increases beyond these optimal values for each sorbent, a general trend of decreasing adsorption capacity is evident. This decline can be attributed to the reduced availability of protons competing for adsorption sites and the possible precipitation of Pb (II) as metal hydroxides at higher pH levels. The results corroborate earlier research reported in the literature [39, 40]. The untreated banana peel (acid condition) exhibited relatively low removal efficiency, with a maximum of 27% at pH 5, indicating limited adsorption capacity. Acid-

activated banana peel showed significantly improved performance, reaching a maximum Pb(II) removal of 78.45% at pH 4, suggesting that acid treatment enhances the availability of active binding sites. Similarly, alkali-activated banana peel displayed a consistent increase in removal efficiency with increasing pH, achieving the highest removal (82.33%) at pH 6, likely due to increased surface negative charge enhancing metal ion binding. Thermally treated banana peel showed moderate performance with peak removal around 45.21% at pH 5, indicating that heat treatment alone is less effective. In contrast, chemico-thermally treated banana peel exhibited the highest Pb(II) adsorption efficiency across all samples, with a remarkable maximum of 88% at pH 4.

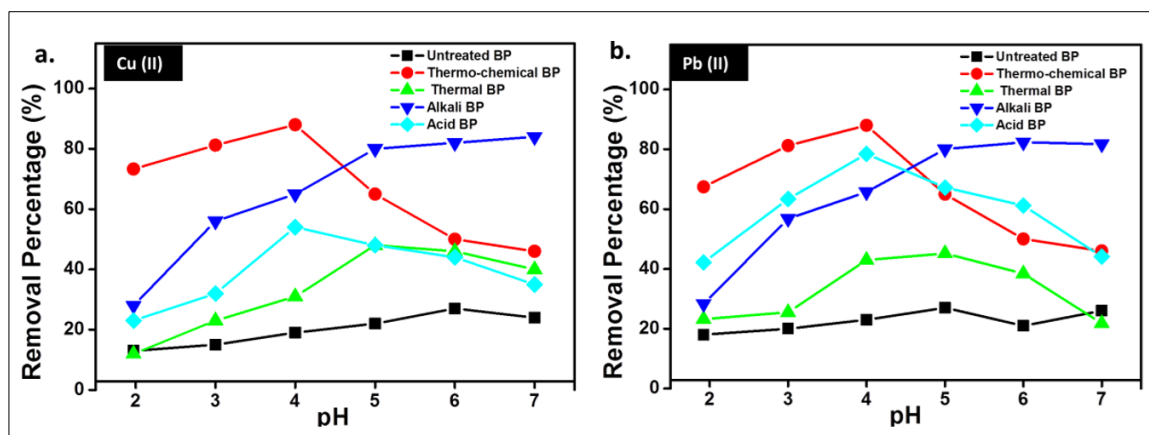


Fig 4: Effect of pH on adsorption of (a) Cu (II) ions and (b) Pb (II) ions for different BP sorbents 3.4a.2. Effect of pH on removal of Pb (II) ions

At low pH levels, only minimal adsorption occurs due to the high concentration and mobility of hydrogen ions (H^+), which compete with toxic metal ions for the available adsorption sites [41]. In these acidic conditions, H^+ ions are preferentially adsorbed onto the sorbent surface, thereby hindering the binding of metal cations. As the pH increases, the concentration of H^+ ions decreases, reducing this competition and allowing more negatively charged ligands on the sorbent surface to become available for binding with metal ions. This results in enhanced adsorption efficiency at moderately higher pH levels. However, under strongly basic conditions (very high pH), metal cations may react with hydroxide ions (OH^-) in the solution, leading to the formation of insoluble metal hydroxides that precipitate out of solution. This precipitation reduces the availability of free metal ions for adsorption, thereby decreasing the overall adsorption capacity. Therefore all sorbents show maximum adsorption at around 4-5 pH levels.

The comparison is more clearly illustrated in Fig 5. Among all the tested sorbents untreated BP, alkali-treated BP (aBP), acid-treated BP (acBP), and thermally treated BP (tBP) the chemically and thermally treated BP (tcBP) exhibits the highest efficiency in the removal of Cu(II) and Pb(II) ions. This enhanced performance can be attributed to the synergistic effects of chemical and thermal modification, which significantly improve the sorbent's surface characteristics. Chemical treatment likely introduces functional groups such as carboxyl, hydroxyl, and carbonyl

onto the biomass surface, increasing its affinity for metal ions. Meanwhile, thermal treatment can enhance porosity and surface area by removing volatile organic compounds and exposing more active sites. Together, these modifications optimize the structural and chemical properties of tcBP, facilitating greater interaction with and binding of metal cations through mechanisms such as ion exchange, complexation, and electrostatic attraction. As a result, tcBP offers a more effective and efficient platform for the adsorption of heavy metals compared to the other treatments.

Effect of contact time on removal of Cu (II) ions

The effect of contact time on the bivalent copper adsorption process on the surface of the untreated BP sorbent and activated BP sorbents at various times in the range of 30-120 min at 30 min intervals was studied, keeping the other parameters fixed (pH 4-5, temperature $40^\circ C$) and the data is tabulated in Table 4.

It is seen in Fig 6a that the removal efficiency of copper ions increased with longer contact time for untreated BP, tBP, acBP and ctBP. The observations are in agreement with existing literature [42, 43]. The chemico-thermally treated peel showed the highest performance, reaching 92.22% removal at 120 minutes, indicating strong adsorption capacity. Untreated banana peel also performed well, with 78.44% removal at 120 minutes, suggesting the natural material has effective binding sites.

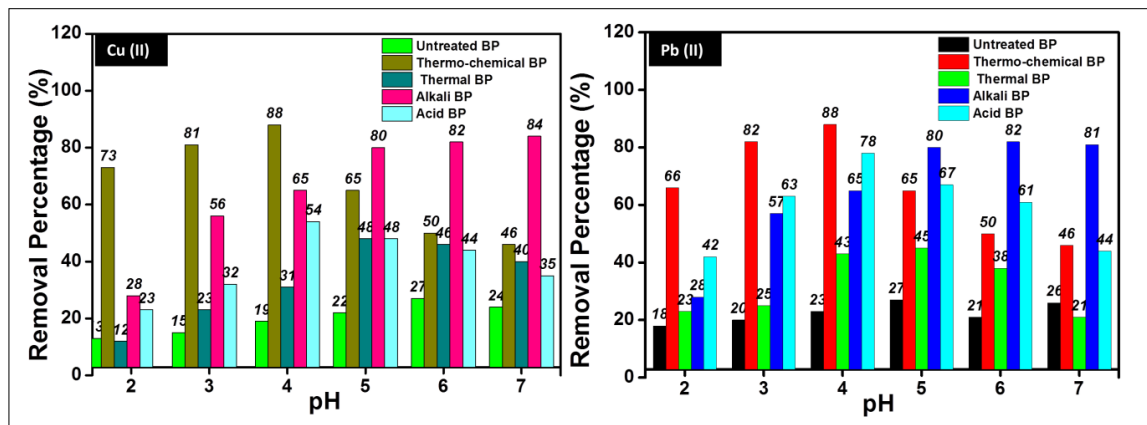


Fig 5: Comparison of the percentage of metal removal using different BP sorbents on adsorption of (a) Cu (II) ions and (b) Pb (II) ions with variation in pH levels

Thermally treated peel showed a steady increase in efficiency, reaching 56.24% at 120 minutes. Acid-treated peel peaked at 64.50% at 90 minutes but dropped afterward, possibly due to desorption. Alkali-treated peel showed the lowest performance, with only 45.44% removal at 120 minutes. Overall, most samples showed improved removal over time, with 120 minutes being optimal for maximum Cu(II) uptake. These findings are attributed to the extended duration allowing more interaction between Cu^{2+} ions and the active sites on the adsorbent surface. Initially, copper adsorption occurs rapidly due to the abundance of easily accessible binding sites. As these sites become occupied, the rate of adsorption slows, and Cu^{2+} ions require more time to diffuse into the inner pores of the adsorbent to locate and bind with the remaining active sites. This time-dependent behavior reflects a typical adsorption process involving both surface interaction and intraparticle diffusion.

Effect of contact time on removal of Pb (II) ions

It is observed that the removal efficiency of lead (Pb^{2+}) ions increases with longer contact time for the untreated BP,

ctBP, acBP, and tBP, the maxima being at 90 mins. This trend suggests that extended contact time facilitates greater interaction between Pb^{2+} ions and the available active sites on the adsorbent surfaces. However, in the case of acid-modified BP, the maximum removal efficiency is achieved at 120 mins, after which a decline in performance is observed, as clearly illustrated in Fig 6b. This reduction may be due to desorption effects, site saturation, or structural changes in the adsorbent over prolonged exposure, which can reduce its binding capacity for lead ions. Untreated banana peel showed the highest removal (88.28%) at 90 minutes, followed by acid-treated peel, which peaked at 84.22% at the same time. Thermally treated peel showed gradual improvement, reaching 58.25% at 120 minutes. In contrast, alkali-treated and chemico-thermally treated peels showed relatively low and inconsistent removal, with maximums of only 40.33% and 56.30% respectively. Most adsorbents reached peak performance around 90 minutes, suggesting it as the optimal contact time for Pb(II) adsorption.

Table 4: Experimentally recorded values for removal% of Cu (II) and Pb (II) ions of different adsorbents with variation in contact time

Percentage removal of Cu (II) on activated banana peel (acid) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.59	28.23
5	60	2.68	46.44
5	90	1.78	64.50
5	120	3.02	39.56
Percentage removal of Cu (II) on activated banana peel (alkali) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.84	23.23
5	60	3.57	28.67
5	90	3.17	36.56
5	120	2.73	45.44
Percentage removal of Cu (II) on activated banana peel (thermally treated) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.73	25.45
5	60	3.39	32.20
5	90	2.73	45.45
5	120	2.19	56.24
Percentage removal of Cu (II) on activated banana peel (chemico-thermally treated) at contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	1.68	66.43
5	60	1.30	74.01
5	90	0.59	88.12
5	120	0.39	92.22

Percentage removal of Cu (II) on untreated banana peel at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	2.01	59.89
5	60	1.68	66.43
5	90	1.38	72.40
5	120	1.08	78.44
Percentage removal of Pb (II) on activated banana peel (acid) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	2.73	45.32
5	60	1.35	73.20
5	90	0.79	84.22
5	120	1.47	70.55
Percentage removal of Pb (II) on activated banana peel (alkali) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.83	23.50
5	60	3.09	38.16
5	90	2.98	40.33
5	120	3.07	38.54
Percentage removal of Pb (II) on activated banana peel (thermally treated) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.29	34.25
5	60	3.10	38.20
5	90	2.96	40.71
5	120	2.09	58.25
Percentage removal of Pb (II) on activated banana peel (chemico-thermally treated) at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	3.58	28.32
5	60	3.48	30.50
5	90	2.19	56.30
5	120	3.34	33.20
Percentage removal of Pb (II) on untreated banana peel at various contact time			
Initial Conc (ppm)	Contact Time (min)	Final Conc (ppm)	Removal%
5	30	1.57	68.66
5	60	1.39	72.30
5	90	0.59	88.28
5	120	0.69	86.10

The adsorption effectiveness of copper (Cu^{2+}) and lead (Pb^{2+}) ions is significantly influenced by the contact time between the adsorbent and the metal ion solution. Experimental results indicate that thermally and chemically activated banana peel demonstrates superior adsorptive properties for copper ions compared to other activation methods as seen in Fig 7. This enhanced performance is likely due to the increased surface area and the improved availability of functional groups created during thermal and

chemical treatment. On the other hand, acid-modified banana peel demonstrates a higher affinity for lead ions, suggesting that acid treatment introduces or enhances specific functional groups that favor the binding of lead over copper. These findings highlight the importance of the type of chemical or physical modification applied to banana peel in tailoring its adsorption properties for specific heavy metal ions.

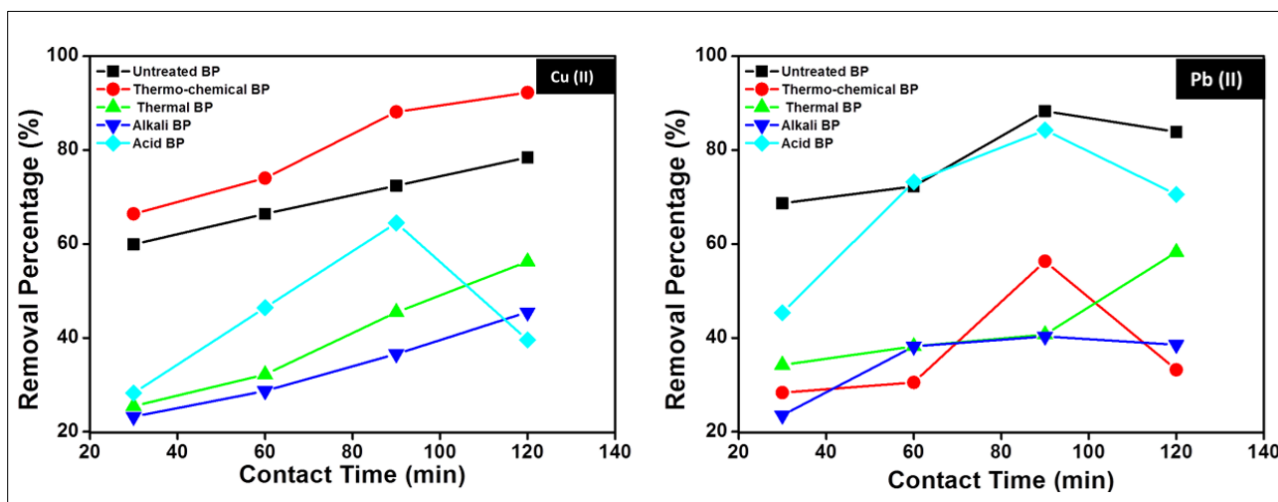


Fig 6: Effect of contact time on adsorption of (a) Cu (II) ions and (b) Pb (II) ions for different BP sorbents

Initial removal of copper and lead ions occurs rapidly upon contact with the adsorbent, as readily available active sites facilitate immediate adsorption. However, as time progresses, and more adsorption sites become active, the metal ions begin to migrate and bind to the most energetically favorable locations. Once the adsorption process reaches equilibrium where all accessible high-affinity sites are occupied the overall rate of adsorption plateaus. At this stage, no significant additional uptake

occurs, and a slight decline in adsorption capacity may be observed, likely due to the cessation of further adsorption activity [44, 45].

The observed reduction in removal efficiency after 90 minutes of contact time is likely attributed to desorption process where previously adsorbed metal ions detach from the adsorbent surface. This is presumed to result from the saturation of available functional groups on the banana peel powder, reducing its capacity to retain metal ions [46].

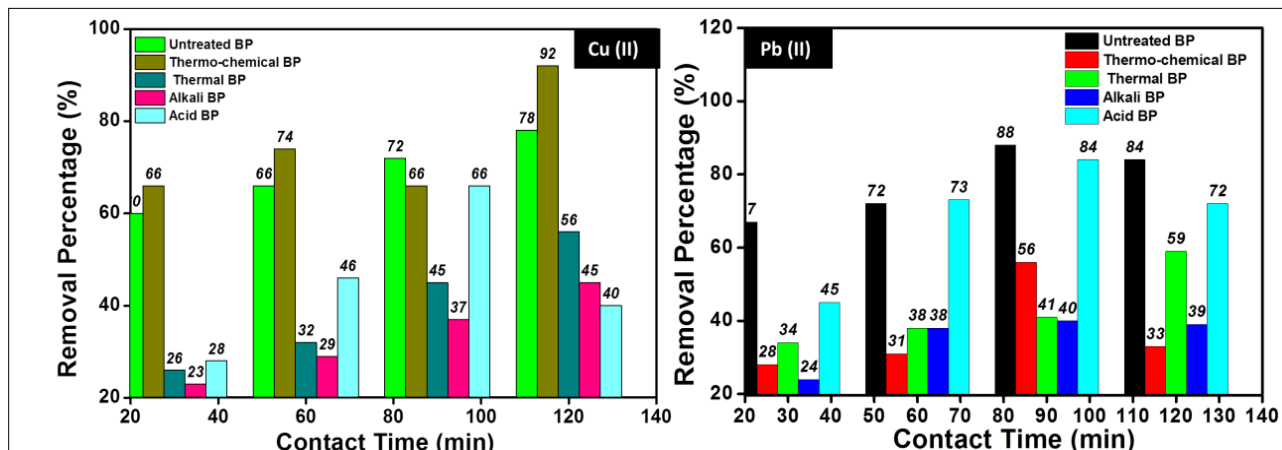


Fig 7: Comparison of the percentage of metal removal using different BP sorbents on adsorption of (a) Cu (II) ions and (b) Pb (II) ions with variation in contact time

Effect of temperature on removal of Cu (II) ions

The influence of temperature on the removal of Cu (II) was studied at various temperatures ranging from 30-50°C. The experimental data is recorded in Table 5, and the data reveals that an improvement in the removal efficiency was recorded with the rise of temperature for acBP, aBP and inactivated BP. Acid-activated banana peel showed the highest removal at 40°C (67.45%), indicating enhanced adsorption with moderate heating. Alkali-treated peel also improved with temperature, reaching 53.66% at 50°C, though still less effective overall. Thermally treated peel showed a strong temperature-dependent trend,

improving from 18.54% at 60°C to 77.40% at 150°C, highlighting the benefit of higher thermal activation. Chemico-thermally treated banana peel achieved maximum removal of 87.50% at 450°C, confirming this as the most effective treatment under high-temperature conditions. In contrast, untreated peel performed poorly across all temperatures, with a maximum of only 23.98% at 50°C. Overall, temperature positively influenced Cu(II) removal, especially for thermally and chemically modified peels, likely due to enhanced diffusion and activation of adsorption sites.

Table 5: Experimentally recorded values for removal% of Cu (II) and Pb (II) ions of different absorbents with variation in temperature

Percentage removal of Cu (II) on activated banana peel (acid) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	3.42	31.55
5	30	1.88	62.32
5	40	1.63	67.45
5	50	2.10	58.01
Percentage removal of Cu (II) on activated banana peel (alkali) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	4.31	13.83
5	30	3.59	28.16
5	40	2.66	46.87
5	50	2.32	53.66
Percentage removal of Cu (II) on activated banana peel (thermally treated) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5.00	60	4.07	18.54
5.00	80	3.57	28.54
5.00	100	2.24	55.21
5.00	120	1.14	73.22
5.00	1000	1.36	76.88
5.00	1500	1.13	77.40
Percentage removal of Cu (II) on activated banana peel (chemico-thermally treated) at various temperatures			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	30	1.82	63.65

5	350	1.74	65.20
5	400	1.18	76.44
5	450	0.63	87.50
5	500	1.58	68.31
Percentage removal of Cu (II) on untreated banana peel at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	4.84	3.13
5	30	4.57	8.61
5	40	4.08	18.44
5	50	3.80	23.98
Percentage removal of Pb (II) on activated banana peel (acid) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	1.88	62.43
5	30	1.20	76.01
5	40	0.79	84.23
5	50	1.82	63.55
Percentage removal of Pb (II) on activated banana peel (alkali) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	4.28	14.32
5	30	3.95	20.20
5	40	3.83	23.44
5	50	3.97	20.56
Percentage removal of Pb (II) on activated banana peel (thermally treated) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5.00	40	3.94	21.25
5.00	60	3.35	33.34
5.00	80	2.35	52.96
5.00	100	1.14	77.20
5.00	120	0.87	82.66
5.00	150	1.05	79.40
Percentage removal of Pb (II) on activated banana peel (chemico-thermally treated) at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	300	2.59	48.20
5	350	1.42	72.00
5	400	1.18	76.44
5	450	0.52	89.52
5	500	1.56	68.71
Percentage removal of Pb (II) on untreated banana peel at various temperature			
Initial Conc (ppm)	Temperature (°C)	Final Conc (ppm)	Removal%
5	20	4.38	12.35
5	30	4.10	18.01
5	40	3.95	21.50
5	50	3.83	23.33

Effect of temperature on removal of Pb(II) ions

Among all treatments, acid-activated banana peel showed the highest removal efficiency, reaching up to 84.23% at 40°C, indicating strong enhancement of adsorption sites through acid activation. Chemico-thermally treated banana peel also exhibited high performance, with maximum removal of 89.52% at 450°C, suggesting a synergistic effect of chemical and thermal activation. Thermally treated samples alone showed increasing removal with temperature, peaking at 82.66% at 120°C, before a slight decline. In contrast, alkali-activated and untreated banana peel demonstrated comparatively low adsorption capacities, with maximum removals of 23.44% and 21.50%, respectively. Overall, acid and chemico-thermal activation proved most effective in enhancing the Pb(II) adsorption potential of banana peel, primarily due to improved surface characteristics and availability of active binding sites.

Elevated temperatures may provide heavy metal ions with sufficient kinetic energy to interact more effectively with the surface-bound functional groups of banana peel powder, thereby enhancing the process of adsorption^[47]. It is also inferred that higher temperature change the interaction area

for the metal ions by expanding the surface area of the adsorbents^[48].

Effect of concentration of acid/alkali on removal of Cu (II) and Pb (II) ions

Variation in the concentration of acid and alkali in activation plays a vital role as observed from the data recorded in Table 6. The removal efficiency of Cu(II) ions by banana peel increased with higher adsorbent concentrations for all activation methods. Among the different treatments, chemico-thermally activated banana peel showed the highest performance, achieving a maximum of 74.21% removal at 50% concentration, followed closely by alkali-activated banana peel, which reached 72.05% under the same conditions. In comparison, acid-activated banana peel exhibited lower adsorption efficiency, with a peak removal of 45.54% at 40% concentration, indicating limited improvement in surface reactivity. The overall increase in removal percentage with concentration suggests that more active adsorption sites became available as the adsorbent dose increased. Thus, the chemico-thermal activation process significantly enhanced the Cu(II)

adsorption capacity of banana peel due to improved porosity and surface functionality.

Among the treatments, chemico-thermally activated banana peel exhibited the highest adsorption efficiency for Pb(II), achieving up to 88.97% removal at 50% concentration, indicating the combined activation greatly enhanced the surface activity and number of binding sites. Acid-activated banana peel showed moderate performance, with a maximum removal of 70.45% at 40% concentration, while alkali-activated banana peel performed slightly better,

reaching 72.33% removal at 50% concentration. The consistent rise in removal efficiency with increasing adsorbent concentration suggests more available active sites for Pb(II) binding, leading to higher metal uptake until saturation is approached. Overall, chemico-thermal activation proved to be the most effective modification technique for maximizing lead ion removal. A comparative analysis of all parameters with relevant literature has been provided in the Supplementary Tables S1 and S2

Table 6: Experimentally recorded values for removal% of Cu (II) and Pb (II) ions of different adsorbents with variation in acid/alkali concentrations.

Percentage removal of Cu (II) on activated banana peel (acid) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	3.89	22.21
5	20	3.58	28.43
5	30	3.15	37.09
5	40	2.72	45.54
5	50	2.98	40.42
Percentage removal of Cu (II) on activated banana peel (Alkali) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	3.10	38.01
5	20	2.28	54.44
5	30	1.74	65.25
5	40	1.58	68.45
5	50	1.40	72.05
Percentage removal of Cu (II) on activated banana peel (chemico-thermally treated) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	3.49	30.29
5	20	2.08	58.34
5	30	1.89	62.12
5	40	1.74	65.30
5	50	1.29	74.21
Percentage removal of Pb (II) on activated banana peel (acid) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	2.73	45.32
5	20	2.29	54.11
5	30	2.18	56.32
5	40	1.48	70.45
5	50	1.57	68.66
Percentage removal of Pb (II) on activated banana peel (alkali) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	3.12	37.63
5	20	2.28	54.33
5	30	1.74	65.12
5	40	1.57	68.64
5	50	1.38	72.33
Percentage removal of Pb (II) on activated banana peel (chemico-thermally treated) at various concentrations			
Initial Conc (ppm)	Concentration (%)	Final Conc (ppm)	Removal%
5	10	1.33	73.32
5	20	1.10	78.01
5	30	0.96	80.88
5	40	0.88	82.32
5	50	0.55	88.97

The comparative enhancements in metal removal efficiency are more prominently observed in the graphs plotted in Fig 8. Variations in chemical concentration directly influence the surface chemistry of the adsorbent, particularly the availability and nature of functional groups that contribute for binding metal ions. This improvement while increasing the acid concentration can be attributed to the acid's ability

to modify the surface structure, possibly by introducing or exposing more functional groups such as carboxyl and hydroxyl groups that facilitate metal ion binding. Alkaline treatment likely enhances the porosity and increases the number of negatively charged sites, improving the electrostatic attraction between the adsorbent and metal cations.

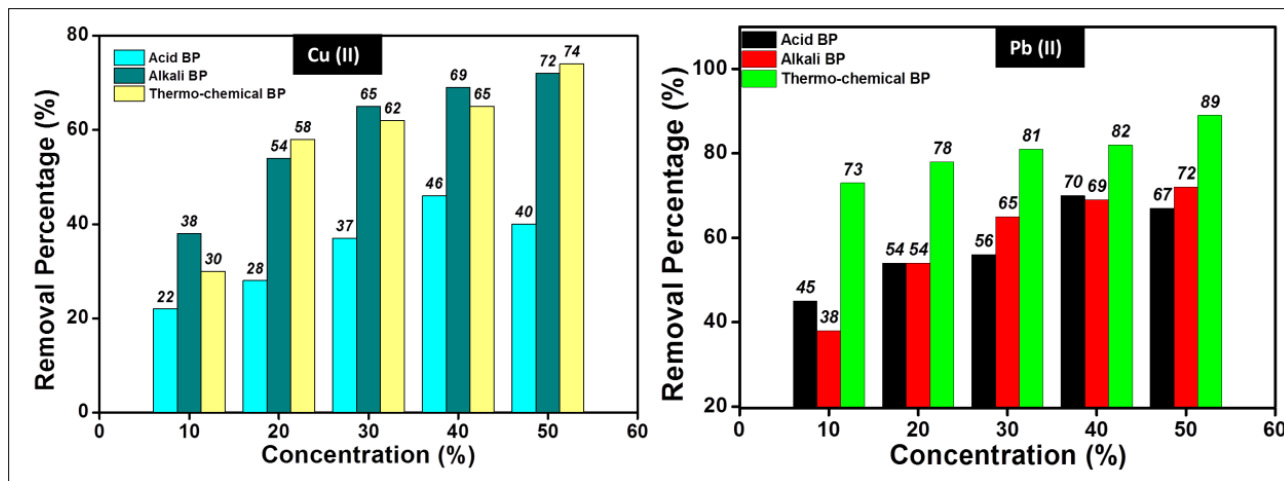


Fig 8: Comparison of the percentage of metal removal using different BP sorbents on adsorption of (a) Cu (II) ions and (b) Pb (II) ions with variation in acid/alkali concentrations.

Kinetic and Isotherm Models

Quantitative kinetic analysis provides valuable insights into the adsorption rate, controlling steps, and overall mechanism of the process. To evaluate the adsorption

kinetics, the pseudo-first-order and pseudo-second-order models were applied, and the corresponding parameters are summarized in Table 7.

Table 7: Experimentally recorded values of kinetic parameters of chemico-thermally activated banana peel

Metal ions,	Kinetic parameters of chemico-thermally treated activated banana peel					
	Pseudo-first-order			Pseudo-second-order		
	k_1 (min ⁻¹)	$Q_{e, cal}$ (mg/g)	R_2	k_2 (min ⁻¹)	$Q_{e, cal}$ (mg/g)	R_2
Cu (II)	0.0172	1.2522	0.9665	1.2835	0.0379	0.9898
Pb (II)	0.0396	2.2451	0.8115	0.0195	2.6345	0.904

The comparison of correlation coefficients (R^2) reveals that the pseudo-second-order model ($R^2 = 0.9898$ for Cu(II) and 0.904 for Pb(II)) provides a better fit to the experimental data than the pseudo-first-order model ($R^2 = 0.9665$ and 0.8115, respectively).

This indicates that adsorption of metal ions onto chemico-thermally treated activated banana peel follows

predominantly pseudo-second-order kinetics. The pseudo-first-order model assumes that the adsorption rate is mainly controlled by the diffusion of adsorbate molecules through the boundary layer. In contrast, the pseudo-second-order model suggests that the rate-limiting step involves chemisorption, characterized by electron sharing or exchange between adsorbent and adsorbate ^[49].

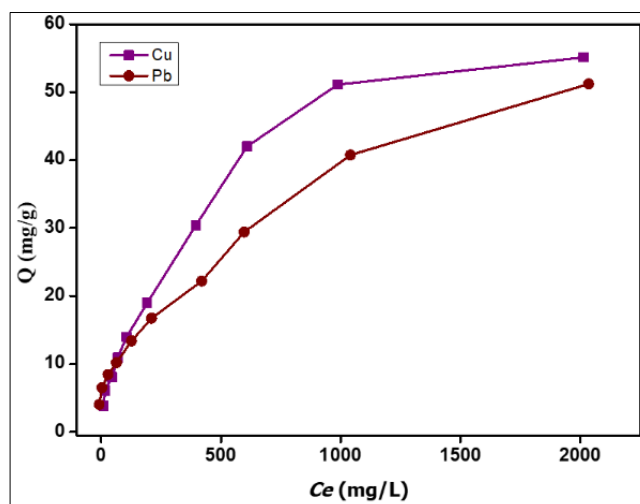


Fig 9: Adsorption isotherms of Cu(II) and Pb(II)

The isothermal adsorption behavior of chemico-thermally treated activated banana peel was investigated in ion solutions with initial concentrations ranging from 0 to 2000 mg/L. The experimental adsorption isotherms for Cu(II) and for Pb(II) ions are presented in Fig 9. It was observed that the adsorption capacity (Q) increased significantly with the

rising initial metal ion concentration at the beginning of the process, indicating that more active sites on the surface became occupied as the ion concentration increased. The adsorption isotherm study explains how metal ions interact with the chemico-thermally treated activated banana peel surface. The equilibrium data were analyzed using

Langmuir and Freundlich models and the parameters are reported in Table 8. The Langmuir model assumes monolayer adsorption on a uniform surface, but low

correlation coefficients ($R^2 = 0.6044$ for Cu(II) and 0.2399 for Pb(II)) and negative constants indicate that the adsorption does not follow this model.

Table 8: Experimentally recorded values of Langmuir and Freundlich parameters of chemico-thermally activated banana peel

Metal ions,	Isotherm parameters of chemico-thermally treated activated banana peel					
	Langmuir			Freundlich		
	Q_m (mg/g)	K^L (L/mg)	R^2	K^f	n	R^2
Cu (II)	-193.4164	-0.0185	0.6044	0.7477	0.5352	0.9848
Pb (II)	-67.7479	-0.0255	0.2399	0.0979	0.3853	0.9326

In contrast, the Freundlich model showed much higher correlation coefficients ($R^2 = 0.9848$ for Cu(II) and 0.9326 for Pb(II)), suggesting that adsorption occurs on a heterogeneous surface through multilayer adsorption. The n values (<1) indicate favorable adsorption at lower concentrations. Thus, the adsorption of Cu(II) and Pb(II) ions onto activated banana peel is best described by the Freundlich isotherm, implying a heterogeneous and chemisorption-controlled process.

Conclusion: This study provides an extensive and comparative analysis on the removal of toxic metal ions of Cu^{2+} and Pb^{2+} using a bio-sorbent made from banana peel when treated with different techniques for activation. The morphological and structural analyses are supported by SEM, FT-IR and XRD. The effect on individual parameters of variation of temperature, contact time, acid/alkali concentration and pH levels was also studied in -depth to find the optimised parameters and best suitable activated banana peel sorbent for efficient removal of toxic ions. The adsorption of Cu(II) and Pb(II) ions by banana peel was strongly influenced by pH, contact time, temperature, and concentration. Optimal removal occurred at pH 4-6, with the chemico-thermally activated peel showing the highest efficiency of 88.02% for Cu(II) and 88% for Pb(II). For contact time, maximum adsorption was observed at 120 minutes, with 92.22% Pb(II) and 88.02% Cu(II) removal. Increasing temperature enhanced adsorption, peaking at 89.52% (Pb) and 87.50% (Cu) for chemico-thermally treated peels at 450°C, while acid- and alkali-treated peels showed moderate performance (84.23% and 53.66%, respectively). Adsorption also increased with concentration, reaching 88.97% (Pb) and 74.21% (Cu) at 50%. Overall, chemico-thermal activation proved most effective, followed by alkali and acid treatments, while untreated and thermally treated peels showed comparatively lower removal. The isotherm and kinetic studies confirmed that the adsorption of Cu(II) and Pb(II) ions onto chemico-thermally treated activated banana peel occurs mainly on a heterogeneous surface and is better represented by the Freundlich model. The high correlation coefficients ($R^2 = 0.9848$ for Cu(II) and 0.9326 for Pb(II)) indicate multilayer adsorption behavior. Furthermore, the adsorption process follows a pseudo-second-order kinetic model, demonstrating that chemisorption governs the overall adsorption mechanism.

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