Bio-adsorbent for PGM recovery using Macadamia Nutshells

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***Abstract*—** The depletion of the sulphide-bearing PGM ores has brought about significant interest in exploring the need to treat oxide-bearing PGM ores, which are discarded and stockpiled. This has led to alternative methods of processing oxide PGM ores as they are not easily recovered via conventional flotation processes. Leaching of oxide PGM ores has led to the study of adsorption techniques to recover PGMs from solutions. Preparation for a bio-adsorbent was conducted using an agricultural waste, macadamia nutshell biomass. Particular attention was paid to the characterization of the raw macadamia nutshells, with XRF, XRD, SEM, FTIR, BET and proximate analysis. Following preparation, macadamia nutshell biomass was subjected to pyrolysis to produce biochar that would be used as an adsorbent for adsorption studies. The XRF analysis of the raw macadamia nutshell showed the presence of the dominant elements such as Fe, Zn, K, Si, Ca, S, Al and Mg, indicating an abundance of inorganic material, which is typical of biomass material. The XRD analysis revealed that the macadamia nutshell had a predominantly amorphous structure, which is typical of the natural organic biomass components of cellulose and lignin. The SEM analysis displayed the surface topography of the raw macadamia nutshell, which is composed of irregular, angular particles with a compact, coarse texture and limited porosity. The EDS results showed that the surface was dominated by 59.86wt % carbon and 39.26 wt% oxygen. The determination of functional groups by FTIR analysis showed the presence of hydroxyl, carbonyl, and hydrocarbon chain groups. Furthermore, the proximate analysis showed the sample exhibited a high content of volatile matter, surpassing 80%, a moderate moisture content of 10-12%, a low fixed carbon content of 6-8% and extremely low ash content of 0.75%. The results obtained from characterization were used to understand the suitability of the biosorbent for PGM adsorption studies.

***Keywords*—** Characterization, Biosorbent, PGMs, Macadamia biochar, Adsorption

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I. Introduction

The fast decline in high-grade and easily processed sulphide PGM-bearing ores has led to the exploration of innovative approaches for the beneficiation of oxidised PGM ores[1].

The successful extraction of sulphide PGM-bearing ores found in the Bushveld igneous complex (BIC) of South Africa is mostly owing to the PGM association with base metal sulphides, whereby conventional processing methods such as flotation are conducted [2].

The near-surface oxidised PGM ores have shown much difficulty when processed by means of conventional methods, which have shown that poor PGM flotation recoveries are due to the complex mineralogy of oxidized ores **Error! Reference source not found.**. These challenges have led to high volumes of oxidized PGM ores estimated at around 500 million tonnes being unmined, discarded, stockpiled and regarded as overburden waste in South Africa 0. This has led to studies investigating alternative methods in recovering PGMs from oxidized ores by means of leaching, which leads to the adsorption of PGMs from the leachate solutions. A suitable requirement for a sustainable biosorbent that effectively adsorbs PGMs from the leachate and has improved adsorption characteristics to adsorb precious metals is essential in improving efficiency and generating an eco-friendly alternative. This study addressed this gap by presenting a detailed characterization of macadamia biomass and biochar, paving the way for efficient adsorption and PGMs recovery.

II. Materials and Methods

A. Materials

The raw, unprocessed macadamia nutshells sample was obtained from a local South African farm in the Limpopo province, South Africa. It was cleaned, washed, dried and ground to a 2-3mm size range. The samples were homogenized and split using a rotary sample splitter. Appropriate samples were then taken as per experiment requirements for characterization and analysis.

B. Methods

The sample was then pulverized to <75 microns and analysed to determine the presence of the functional groups using the Fourier transform infrared spectroscopy (FTIR) equipment. The sample analysed for chemical composition was prepared using 10g of sample with 5g of binder (Sasol wax) and then pelletizing. The mineralogical phases of the sample were determined using Rigaku Ultima IV X-ray diffraction (XRD) analysis equipment. The Tescan Vega

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3Xmu scanning electron microscopy (SEM) was used to analyse the surface morphology and energy dispersive X-ray spectroscopy (EDS) was used to determine the chemical elements and elemental weight percentages. The surface area, pore volume and pore size were determined by the Brauner Emmet Teller (BET) analyser instrument. The proximate analysis was conducted to determine the fixed carbon content of the macadamia biomass after the volatile matter, moisture content and ash had been removed from the sample using the muffle furnace at various operating temperatures.

III. Results And Discussion

The analysis of the macadamia nutshell sample was conducted prior to and after pyrolysis to investigate the effects of three pyrolysis temperatures (450°C, 550°C & 650°C).

A. Chemical composition results of macadamia samples

The chemical composition of the macadamia samples was determined using XRF and the results are shown in Table 1. According to Table 1, the main elements were Fe, Zn, K, Si, Ca, S, Al and Mg. Other trace elements were detected at ≤ 1%. Table 1 shows the XRF analysis results of the biochar at 450°C, revealing a remarkable redistribution and concentration of inorganic components that fundamentally alter the mineral composition profile.

TABLE I
ELEMENTAL COMPOSITION OF DIFFERENT TEMPERATURES AFTER PYROLYSIS

Raw sample	**Element**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**C**	
	wt(%)	0.00	1.93	2.46	5.93	0.45	4.08	4.57	
	Element	**K**	**Ca**	**Cr**	**Mn**	**Fe**	**Zn**	**Pb**	
	wt(%)	7.69	4.94	1.67	0.60	21.00	8.77	0.81	
450°C	**Element**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	
	wt(%)	4.78	1.97	1.07	1.82	0.77	2.64	0.92	
	Element	**K**	**Ca**	**Mn**	**Fe**	**Cu**	**Zn**	**Rb**	
	wt(%)	22.41	20.19	2.67	10.27	0.63	0.51	0.14	
550°C	**Element**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	
	wt(%)	4.67	2.34	0.78	1.39	0.81	2.66	0.67	
	Element	**K**	**Ca**	**Cr**	**Mn**	**Fe**	**Cu**	**Zn**	
	wt(%)	21.86	20.85	0.58	4.34	5.11	0.75	0.51	
650°C	**Element**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**
	wt(%)	6.17	2.23	0.62	1.24	0.71	2.47	0.89	23.21
	Element	**Ca**	**Cr**	**Mn**	**Fe**	**Cu**	**Zn**	**Rb**	**Zr**
	wt(%)	18.57	0.44	4.10	5.53	0.55	0.42	0.12	0.22

B. Mineral Phases of the raw Macadamia nutshells

Fig. 1 represents the XRD spectra of the raw macadamia nutshell biomass. The sample showed mineral phases identified as cellulose, silicon oxide and cellulose. This agrees with the XRF analysis. The dominant phase, cellulose, is of organic composition (C, H, N, O). The XRD pattern displayed an amorphous structure, which is distinctive of dominant organic material such as biomass. The low intensity of mineral phases of the macadamia biomass is due to its mineral phase as amorphous because of the presence of (C, H, N, O) that inhabit the nutshell structure and cellulose arrangement. The presence of other oxides, including Na_2O (6.45 mass%), MgO (3.27 mass%), Al_2O_3 (2.02 mass%), P_2O_5 (1.76 mass%), and MnO (3.45 mass%) indicates a diverse mineral composition that became more prominent following organic matter removal.

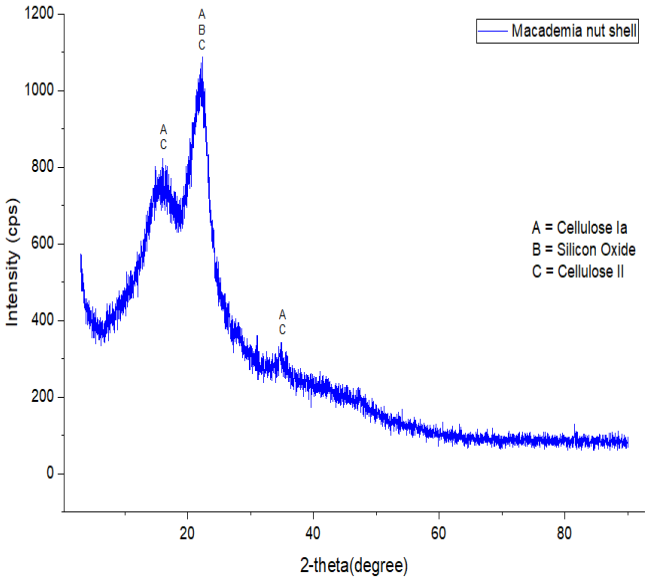

Fig. 1 XRD spectra of macadamia biomass before pyrolysis

C. Surface Morphology of the Macadamia nutshell samples – SEM

The SEM (AA) image shows the surface of a raw macadamia nutshell that is composed of irregular, angular particles with a dense, rough texture and limited visible porosity. This structure is typical for unprocessed lignocellulosic biomass. Table 3 represents the EDS results that indicate that the surface is dominated by carbon (59.86 wt%) and oxygen (39.26 wt%), aligning with the organic nature of biomass composed of cellulose, hemicellulose, and lignin. Trace amounts of elements such as Na, Mg, Al, Si, P, S, Cl, K, and Fe were also detected.

The surface elemental composition, represented in Table 4, shows a significant increase in carbon content to 81.24 wt% from the original 59.86 wt%, with a corresponding decrease in oxygen content to 16.71 wt% from 39.26 wt%. The trace elements (Na, Mg, S, K, and Ca) detected by EDS show notable concentration effects, with potassium increasing dramatically from 0.07 wt% to 1.25 wt% and calcium appearing prominently at 0.37 wt%, while sodium rises to 0.23 wt%.

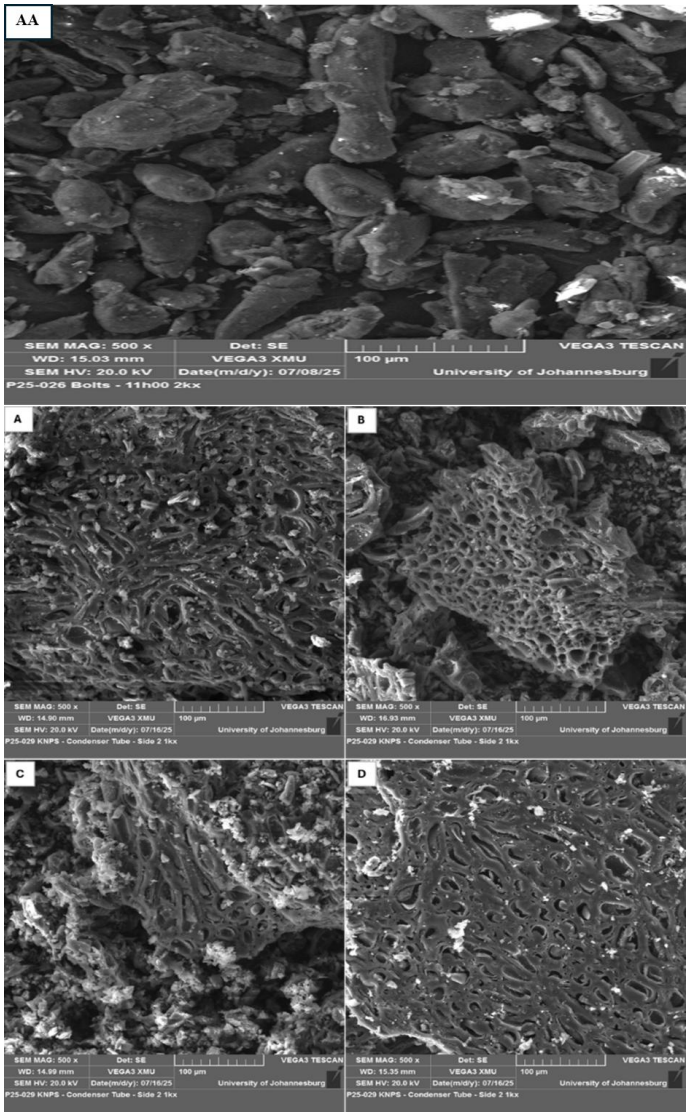

Fig 2 Morphology results of macadamia material before and after Pyrolysis at various temperatures

Fig. 2 shows the SEM analysis results that reveal a further maturation of the porous structure, where the biochar maintains its highly developed porosity while exhibiting a more organized and refined pore structure compared to the 450°C sample. Interestingly, the elemental composition shows a slight but noteworthy shift, with carbon content decreasing marginally from 81.24 wt% at 450°C to 80.50 wt%, while oxygen content increases from 16.71 wt% to 18.96 wt%.

From the SEM results shown in Fig. 2 (A), it is visible that the surface morphology has undergone a dramatic transformation from the original dense, compact structure to a highly porous, honeycomb-like matrix with well-developed pore networks and irregular, fragmented surfaces. The surface elemental composition, represented in Table 4, shows a significant increase in carbon content to 81.24 wt% from the original 59.86 wt%, with a corresponding decrease in oxygen content to 16.71 wt% from 39.26 wt%. The trace elements (Na, Mg, S, K, and Ca) detected by EDS show notable concentration effects, with potassium increasing dramatically from 0.07 wt% to 1.25 wt% and calcium appearing prominently at 0.37 wt%, while sodium rises to 0.23 wt%.

The SEM image (B) shows a surface morphology that continues to evolve from earlier temperatures, now exhibiting a more consolidated and structured porous network. The pores appear better defined and interconnected, indicating continued volatilization of organic content and collapse of weak biomass structures, which results in a more refined carbon framework. Elemental analysis represented in Table 4 confirms a significant degree of carbonization, with carbon content reaching 84.32 wt%, the highest among the intermediate temperature ranges.

The image (D) shows the SEM analysis of biochar produced at 650 °C which shows a surface that has undergone near-complete carbonization, with the development of a well-defined porous architecture that is more refined and consolidated than at lower temperatures. Elemental composition reflects this advanced carbonization, with carbon content peaking at 92.20 wt%, while oxygen content drops dramatically to just 7.51 wt%. This agrees with the FTIR spectrum (Fig. 2), which shows loss in functional groups due to thermal degradation, which leads to dehydration and carbonization[6].

The dominance of K_2 O and CaO across all temperatures, with both oxides showing peak concentrations at intermediate temperatures: K_2 O reaches maximum values around 550°C (29.14 mass% at 500°C and 26.34 mass% at 550°C), Iron oxide (Fe_2 O_3) shows an interesting pattern, decreasing from 450°C to 550°C, then increasing again at 550°C and 650°C, suggesting complex phase transformations and volatilization-concentration dynamics. Silicon dioxide (SiO_2) consistently decreases with increasing temperature, from 3.89 mass% at 450°C to 2.65 mass% at 650°C, indicating progressive volatilization of silicate phases. Sulphur content (SO_3) shows a general declining trend with some fluctuations, reflecting the thermal decomposition of sulphur-containing compounds, while other minor oxides exhibit varying patterns that suggest different thermal stabilities and transformation behaviors.

Although more heat (550–650°C) produces higher carbon content and more-developed porosity, 450°C biochar offers an optimum balance for adsorption conditions, particularly when both chemical and physical adsorption are needed. Oxygen functionality retention at 450°C and a moderate extent of carbonization, reflected by SEM-EDS, suggests that this biochar possesses sufficient structural stability for environmental use, and active surface chemistry required for interaction with a diverse range of contaminants.

Moreover, the mineral content at 450°C, as determined from XRF, consists of a wide range of suitable oxides like Fe_2 O_3 , ZnO, and K_2 O that support cation exchange, complexation, and surface precipitation processes. These substances, together with accessible surface functional groups, make 450°C biochar an effective option for the removal of heavy metals, dyes, and other polar pollutants from aqueous solutions.

On the other hand, biochar generated at higher temperatures (specifically 650°C) tends to be graphitized and more chemically inert and is therefore less likely to be involved in reactive adsorption processes, yet great for physical

adsorption [5]. Although such material can still be valuable for physical adsorption or filtration-type uses, chemical sorption or ion exchange use may be reduced. The 500 °C and 550°C (Image C) biochar, while showing increases in porosity and mineral content, exhibit reduced functional groups and contain potential volatilization-related inconsistency that would compromise repeatability and performance in sensitive adsorption uses.

D.Functional Groups results

The raw macadamia nutshell biomass was analysed with FTIR equipment to determine the functional groups and the results are shown in Fig.3. Functional groups such as hydrocarbon chains, hydroxyl, carboxyl and carbonyls were identified in the sample. The macadamia biomass results show the occurrence of a peak in the diagnostic region at approximately 3421.86cm^{-1} wavelength. The transmittance table for FTIR results interpretation shows this wavelength strongly indicates the presence of -OH bonds, which is the functional group for hydroxyls, as well as the presence of C-H bonds in the region of 2926.87cm^{-1}, which is the functional group for hydrocarbons. It can be concluded that the functional groups are in alignment with the organic nature of lignocellulosic components found in biomass [6].

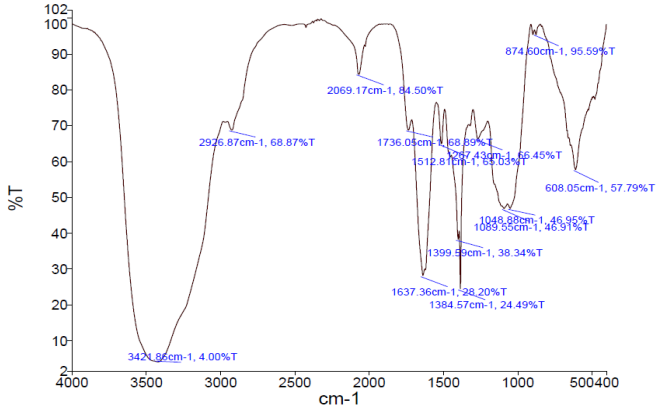

Fig. 3 FTIR spectra of macadamia biomass before Pyrolysis

The FTIR spectrum (Fig. 4) shows the functional group present at 450, 550 and 650°C and what was formed after pyrolysis. The FTIR spectrum of the biochar at 450°C demonstrates evidence of chemical transformation during thermal treatment. A significant removal of hydroxyl is observed, while decomposition and volatilization of hydrocarbon chains and aliphatic compounds are also observed. Complete thermal breakdown of oxygen-containing functionalities is suggested by the indication. The aromatic C=C bands at 1637cm^{-1} and 1512cm^{-1} show reduced intensity, though some aromatic character persists in modified form, indicating partial decomposition of the lignin structure. The complex fingerprint region between 1384-1048cm^{-1}, previously rich with C-O stretching vibrations from polysaccharide structures, has been dramatically simplified with residual peaks remaining. The FTIR spectrum at 550°C shows a continuation of the progressive functional group elimination observed at lower temperatures, confirming a transition toward advanced carbonization. The spectrum demonstrates significant flattening across the wavenumber range. The broad O-H stretching band around 3400-3500 cm^{-1} and aliphatic C-H stretching vibrations in the 2800-3000 cm^{-1} region, both still faintly visible at 450˚ and now virtually absent. This indicates almost complete dehydration and volatilization of hydrocarbon chains and hydroxyl groups. The carbonyl (C=O) absorption region around 1700-1750 cm^{-1} and aromatic C=C stretching bands are barely detectable, suggesting extensive decomposition of carboxylic acids, esters, and lignin-derived aromatic structures. The FTIR spectrum of the 550˚C further reinforces the progressive transformation observed through SEM and EDS. The FTIR spectrum at 650˚C provides clear evidence that the material has reached a graphitic-like state, characterized by an almost completely featureless spectral profile. There are no discernible absorption peaks across the entire wavenumber range, indicating the total elimination of all organic functional groups. The O-H stretching band in the 3400-3500cm range, which was significantly reduced at 550°C, is now completely absent, confirming the loss of hydroxyl groups and the final phase of dehydration. Similarly, the aliphatic C-H region (2800-3000 cm^{-1}) and the carbonyl region (1700-1750 cm^{-1}) show no activity, reflecting the complete breakdown and volatilization of hydrocarbon chains, esters, acids and other oxygenated species. The fingerprint region (1000-1400 cm^{-1}) is flattened, suggesting that all cellulose and hemicellulose-derived functionalities have been destroyed. The thermal degradation creates a highly porous structure with a large specific surface area that is crucial for good adsorption.

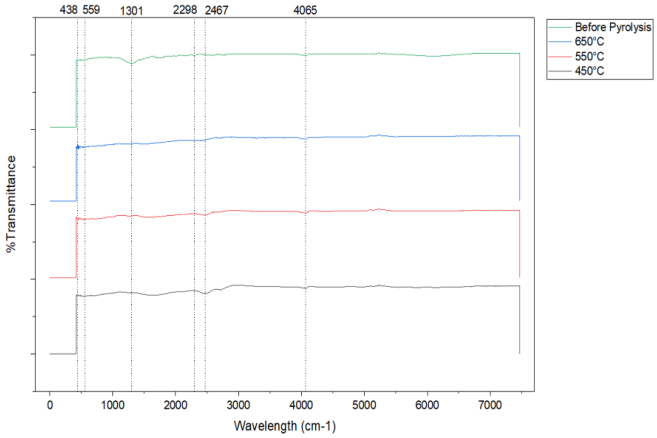

Fig. 4 FTIR spectra of different temperatures after pyrolysis

E. Proximate Analysis

The proximate analysis results (Table II) of the raw macadamia nutshell sample provide a clear indication of its composition prior to pyrolysis. The sample exhibited a very high volatile matter content, exceeding 80%, a moderate moisture content of around 11%, low fixed carbon, and an extremely low ash content. The most prominent observation from the proximate analysis is the dominance of volatile matter, accounting for over 80% of the sample. This indicates that the macadamia nutshell is primarily composed of organic compounds, particularly cellulose, hemicellulose, and lignin.

TABLE II
PROXIMATE ANALYSIS OF MACADAMIA NUTSHELLS

Fixed carbon	Moisture	Ash	Volatile Matter
6.85%	11.00%	7.51%	81.40%

F. Brunauer Emmett Teller (BET) surface area analyser

The sample was analysed using BET and the results are shown in Table III. The negative surface area value of the raw macadamia nutshell demonstrates that the BET equipment was unable to respond to the biomass before pyrolysis, as there were no signs of pores formed or openings for BET analysis to occur. According to the BET surface area measurements, there was a trend that was observed as the temperature increased, the surface area of the 450°C temperature range was observed at 207, 5300 m^2/g, 550 °C at 392, 8075 m^2/g surface area and 650°C was at 439, 5654 m^2/g surface area. There was a significant increase in surface area as the temperature increased from 450°C to - 650°C. The high BET specific surface area indicates that the macadamia biochar formed a highly porous stage due to the pyrolysis temperature increase and maximizes the available sites for adsorption. The pore size of the biochar was observed to be 2.27 nm for 450°C, 2.24 nm for 550°C and 2.37 nm for 650°C. The pore sizes have a close range from 2.2-2.4 nm, which demonstrates slight consistency within this temperature range and leads to mesopores that fall in the range of 2-50 nm. Mesopores are excellent for providing fast transport channels, allowing for adsorbate molecules to quickly diffuse through the biochar and result in high adsorption capacity and fast adsorption [7]. The BET results are in agreement with the SEM-EDS results, as an increase in surface area as the temperature rises. They also correspond with the SEM imaging of a highly porous structure developing as the temperature rises.

TABLE II
THE SURFACE AREA ANALYSER RESULTS

Standard	Surface Area	Pore Volume	Pore size
Raw Macadamia	-0.9682 m^2/g	0,14446 cm^3/g	-5, 9677A/
450˚C	297, 5300 m^2/g	0.19850 cm^3/g	26,687A/2,2687nm
550˚C	392, 8075 m^2/g	0.219950cm^3/g	22,398A/ 2, 2398nm
650˚C	439, 5654 m^2/g	0.260034cm^3/g	23,663A/ 2, 3663nm

IV. CONCLUSION

The comparative analysis of macadamia nutshell biochar produced at different pyrolysis temperatures (450, 550 and 650°C revealed a systematic progression of structural and compositional transformation that provides valuable insights into optimizing biochar properties for adsorption. The SEM-EDS analysis demonstrates a clear evolution in carbon enrichment across the temperature range, with carbon content progressively increasing. This trend indicates that carbon enrichment is not strictly linear with temperature, suggesting complex thermal decomposition processes where certain temperatures ranges may favour the removal of specific carbon-containing compounds. The morphological evolution observed through SEM imaging shows consistent development of porosity across all temperatures, particularly at 550°C and 650°C, where the biochar exhibits well-consolidated yet highly porous architectures that balance structural integrity with surface area development. The FTIR spectroscopic analysis reveals a systematic elimination of functional groups with increasing temperature, providing clear evidence of progressive carbonization. This progressive functional group elimination suggests that lower temperatures preserve more chemically active surface sites, while higher temperatures produce biochars with predominantly physical adsorption characteristics due to reduced surface functionality.

Although more heat (550–650°C) produces higher carbon content and more-developed porosity, 450°C biochar offers an optimum balance for adsorption conditions, particularly when both chemical and physical adsorption are needed. The findings confirm that the macadamia biochar represents an effective, sustainable and viable alternative as a biosorbent for PGM recovery.

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