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Optimization by design of experiments of the preparation of biochar from olive pomace and its physicochemical characterizations

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ABSTRACT

The main objective of this research was to optimize the biochar production process using olive pomace waste through a comprehensive 3-factor design of experiments with a Full Factorial Design model. The study focused on examining the individual effects of three crucial factors: biomass size, reactor temperature, and pyrolysis reaction time on biochar yield, employing a 1st degree polynomial mathematical model. The results highlighted the significant influence of these factors on the pyrolysis process. Moreover, the elaborated biochars underwent extensive physicochemical analyses, including Scanning Electron Microscope coupled with Energy Dispersive X-Ray (SEM/EDX) and X-ray diffraction (XRD), and porosity parameters were determined using the Brunauer–Emmett–Teller method (BET). Stressing the importance of precise factor control, the research emphasized achieving higher biochar yields and promoting sustainability in production. Overall, this study provides valuable insights into biochar production, offering valuable guidance for future research to enhance its environmental applications.

1. Introduction:

The cultivation and processing of olives and olive oil hold a pivotal role in the Mediterranean agricultural landscape, contributing significantly to its industrial, economic, and social sectors **[1]**. Over the past few decades, the introduction of intensive olive orchards, extensive mechanization, and advancements in production techniques have led to a remarkable upsurge in both olive oil and table olive output **[2]**. This surge in olive oil production, however, has given rise to a consequential byproduct in the form of substantial waste generated during the production process. While recent technological advancements have succeeded in reducing the volume of process wastewater, there has been a concurrent increase in the generation of solid waste, known as pomace **[3-4]**.

In recent years, scientists and researchers have embarked on exploring innovative methods for addressing the issue of olive waste, particularly by harnessing the potential of pomace-derived products and biochars originating from olive residues and other waste materials **[5-6]**. Biochar, a porous carbon-rich material, is derived from thermochemically treating organic substances in the presence or absence of oxygen. This process involves various techniques such as pyrolysis, gasification, torrefaction, hydrothermal carbonization, and microwave heating, each characterized by distinct temperature and duration

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parameters **[7-9]**. As a cost-effective and environmentally friendly adsorbent, biochar plays a crucial role not only in waste management but also in carbon capture and storage endeavors, contributing to the reduction of atmospheric CO_2 levels by storing carbon in a stable form during its production **[10]**. The porous structure of biochar is enriched with a multitude of surface functional groups, rendering it highly valuable for applications such as water purification, soil enhancement, clean energy production, and mitigation of greenhouse gas emissions **[11]**. Moreover, biochar exhibits potential for transformation into activated carbon through thermal and chemical processes. Additionally, it can be infused with mineral or organic compounds to create hybrid or functionalized biochars, thereby amplifying its surface area, porosity, and adsorption capabilities **[12]**. The applicability of biochar for diverse purposes hinges on its inherent properties. Biochars possessing elevated electrical conductivity, porosity, and stability at lower temperatures are favored for employment as electrode materials in microbial fuel cells. Variants rich in structurally bound oxygen groups find utility in direct carbon fuel cells. For the development of supercapacitors, biochars characterized by high porosity and structural bound nitrogen groups are particularly desirable. In the realm of soil amendments, biochar with substantial surface area and low ash content holds promise, although the intricate relationship between biochar properties and its suitability as a soil enhancer requires further elucidation **[13]**.

Pyrolysis emerges as the most prevalent method for biochar production. This process can be categorized into two main types: slow pyrolysis and fast pyrolysis. Slow pyrolysis, often referred to as conventional carbonization, involves the gradual heating of biomass at a low rate, resulting in a longer residence time (spanning several days). This method, which has been employed for centuries, is renowned for producing charcoal. In contrast, fast pyrolysis operates at high heating rates (exceeding 200 K/min) and shorter residence times (less than 10 seconds), leading to higher yields of bio-oil and a distinct ratio of biochar production **[14-15]**.

This research endeavor seeks to delve into the optimization effects of several key parameters on the production of biochar from solid olive pomace waste. Factors such as biomass size, pyrolysis temperatures, and pyrolysis duration will be systematically investigated to discern their influence on the yield, physical characteristics, and chemical properties of the resulting biochar. By scrutinizing these variables, this study aims to unlock insights that could pave the way for more efficient and sustainable utilization of olive waste materials, contributing to the continued evolution of the olive oil industry while simultaneously addressing environmental concerns.

2. Material and methods:

2.1. Feedstock material:

The olive pomace, originating from the 2022 harvest of the Picholine olive variety, was generously supplied by a local oil mill situated in Khenifra (Morocco). This establishment employs a traditional three-phase extraction process, utilizing rotating stones to facilitate the extraction of olive oil. In order to prepare the pomace for subsequent applications, a rigorous washing regimen was meticulously executed, employing distilled water. Through a series of washing cycles, the objective was to effectively eliminate soluble organic components adhering to the surface of the marc. Following the comprehensive washing procedure, the treated olive pomace underwent a precisely controlled drying process. This drying phase was carried out within an oven, the temperature of which was set at 60°C, and this process continued for a duration of 72 hours. The primary aim of this carefully monitored drying procedure was to substantially reduce the moisture content of the pomace, thereby enhancing its suitability for a diverse range of applications. Upon completion of the drying stage, the olive pomace underwent a meticulous sieving procedure to achieve the desired particle size. Specifically, the process ensured the creation of two distinct phases: one with particles below 2 mm and another with particles exceeding 2 mm. This particular size specification was chosen with the intention of optimizing the pomace for its intended utilization in subsequent processes.

2.2. Pyrolysis procedure:

Pyrolysis investigations were meticulously carried out using a vertically oriented stainless-steel reactor. The biomasses sourced from olive pomace were precision-placed within tightly sealed stainless-steel containers, each equipped with perforations. These specialized containers underwent pyrolysis within the reactor, with scrupulous adherence to the precise parameters stipulated by the optimization conditions. This entailed subjecting the biomasses to a dynamic temperature range spanning from 400°C to 500°C, with corresponding time intervals ranging from 1 to 2 hours. The entire heating process was executed at a consistent and controlled rate of 5°C per minute. To ensure the robustness and reliability of the findings, the complete experiment was rigorously replicated three times. Upon the culmination of the carbonization process, the resultant biochar material was diligently collected. These biochar samples were subsequently carefully stored within glass jars, and each jar was meticulously labeled. This comprehensive labeling approach was adopted to facilitate the seamless identification and accurate tracking of individual samples throughout the subsequent phases of the study.

2.3. Optimization by design of experiments:

The design of experiments methodology was employed to systematically optimize the experimental parameters governing the biochar preparation process **[16]**. The yield of the biochar was adopted as the representative parameter to gauge the effectiveness of the pyrolysis reaction. Employing a full factorial design matrix, the optimization process centered around three distinct factors, labeled as X_i:

- Factor 1 = *BS*: biomass size (<2mm and >2mm);
- Factor 2 = *RT*: Reactor temperature (400°C and 500°C);
- Factor 3 = *PT*: Pyrolysis reaction time (2h and 5h).

In the context of this design matrix, each factor was assigned two levels, with the high level coded as +1 and the low level coded as −1. The total number of tests conducted accounted for k factors.
In the analysis, the following terms were employed:

$$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n}\sum_{j=1}^{n-1} a_{ij} X_i X_j + a_{ijk} X_i X_j X_k$$

With:

- a_0: Mean:
- a_i: 3 effects for each factor;
- a_{ij}: 3 effects present the interactions of 2nd order;
- a_{ijk}: 1 effect presents the interactions of 3rd order.

By systematically exploring these factors and their interactions, we aimed to elucidate the underlying relationships and optimize the biochar preparation process, ultimately enhancing its efficiency and yield.

2.4. Physicochemical characterization:

The biochar samples, following the optimization process, underwent comprehensive characterization through a range of analytical techniques. Surface morphology and elemental compositions were carefully assessed utilizing scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray spectroscopy (EDS), these analyses were conducted using a JSM-5800 device manufactured by JEOL Ltd., based in Tokyo, Japan. To delve into the crystalline phase structure, X-ray Diffraction (XRD) was employed, this investigation was carried out using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation (wavelength: 1.54 Å), manufactured by Bruker Corporation situated in Billerica, MA, USA. Furthermore, critical parameters related to the materials' porous characteristics were determined. Total pore volume (V_{Total}), pore diameter (D_p), and BET surface areas (S_{BET}) were estimated utilizing a Micrometrics ASAP 2020 analyzer, which is developed by Micromeritics Instrument Corporation located in Norcross, GA, USA. This analysis was conducted by examining the nitrogen adsorption-desorption isotherm at a temperature of 77 K.

2.5. Statistical analysis:

The statistical evaluation of the test outcomes was carried out employing the XLSTAT toolbox (2016), an extension integrated with Microsoft Excel 13 software. The obtained values are displayed as the mean accompanied by its corresponding uncertainty, all determined at a significance level of 5%. The statistical analysis was conducted utilizing the Student’s t-test methodology, and each experimental variant was subjected to a triad of replications. In essence, the statistical assessment of the test results was facilitated through the utilization of the XLSTAT toolbox (2016), a supplementary component harmoniously integrated with the Microsoft Excel 13 software. The representation of values is achieved by indicating the mean alongside its associated level of uncertainty, derived under a significance threshold of 5%. The statistical scrutiny was executed employing the established Student’s t-test approach, with each distinct experimental condition being subjected to a set of three repetitions.

3. Results:

3.1. optimization of biochar production:

The biochar elaboration process was optimized using a complete 3-factor design of experiments with 8 well-defined experiments in the model. Table 1 displays the performance of each experiment at the pre-selected levels.

Table 1. Yield Y obtained for each test in all experiments.

Bioachar	Factor 1	Factor 2	Factor 3	Response
	BS	**RT**	**PT**	**Y**
	mm	°C	h	%
B1	-1	-1	-1	45.52

B2	-1	-1	1	42.11
B3	-1	1	-1	41.87
B4	1	1	-1	39.12
B5	1	1	1	35.97
B6	1	-1	1	36.8
B7	-1	1	1	36.77
B8	1	-1	-1	41.23

Based on the results obtained, a 1st-degree polynomial mathematical model was developed, incorporating the factors, second-order interactions, and third-order interactions of the 3 factors. The equation below presents the coefficients of the yield model.

$$\boldsymbol{Y = 39.92 - 1.64BS - 1.49RT - 2.01PT + 0.75(BS*RT) + 0.11(BS*PT) - 0.05(RT*PT) + 0.37(BS*RT*PT)}$$

The average yield achieved through the optimization route was 39.92%. The coefficient estimate represents the expected change in response for every unit change in factor value while keeping all other factors constant. The intercept in an orthogonal design represents the overall average response of all runs, and the coefficients adjust around that average based on the factor settings. A Variance Inflation Factor (VIF) of 1 indicates orthogonality among the factors. VIFs greater than 1 suggest multi-collinearity, with higher VIF values indicating more severe factor correlations. Generally, VIFs below 10 are tolerable. The investigation of the three factors individually on the pyrolysis process showed that they considerably decrease the yield, indicating a positive impact on the pyrolysis reaction when the biomass size, reactor temperature, and pyrolysis reaction time are appropriately controlled.
Table 2 presents the statistical parameters of the design experiments model. The Predicted R^2 of 0.0903 is quite distant from the Adjusted R^2 of 0.9005, differing by more than 0.2. This discrepancy might indicate a significant block effect or a potential issue with the model and/or data, warranting consideration of model reduction, response transformation, outliers, etc. It is essential to perform confirmation runs for all empirical models to test their validity. A_{deq} Precision, measuring the signal-to-noise ratio, is desirable to be greater than 4. Your ratio of 10.479 indicates an adequate signal, suggesting that this model can be effectively used to navigate the design space.

Table 2. Parameters statistics of design experiments model.

Model	**Mean of Yield (%)**	**Standard deviation (%)**	**Coefficient of variation (%)**
Full Factorial Design	39.92	1.05	2.63
Coefficient of determination R^2	**Adjusted R^2**	**Predicted R^2**	**A_{deq} Precision**
0.9858	0.9005	0.0903	10.4787

Table 3 presents the statistical parameters of the polynomial yield model. The Model F-value of 11.56 implies that the model is not significantly different from the noise. There is a 22.14% chance that an F-value of this magnitude could occur due to noise. P-values less than 0.0500 indicate significant model terms, but in this case, there are no significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (excluding those necessary to support hierarchy), model reduction might enhance the overall model performance.

Table 3. Statistical parameters of the polynomial model of yield.

Source	**Sum of squares**	**df**	**Mean squares**	**F-value**	**p-value**	
Model	76.47	6	12.75	11.56	0.2214	not significant
A-BS	21.62	1	21.62	19.60	0.1414	-
B-RT	17.79	1	17.79	16.13	0.1553	-
C-PT	32.36	1	32.36	29.35	0.1162	-
AB	4.58	1	4.58	4.15	0.2905	-
AC	0.1081	1	0.1081	0.0981	0.8068	-
BC	0.0210	1	0.0210	0.0191	0.9127	-
Residual	1.10	1	1.10	-	-	-
Cor Total	77.57	7	-	-	-	-

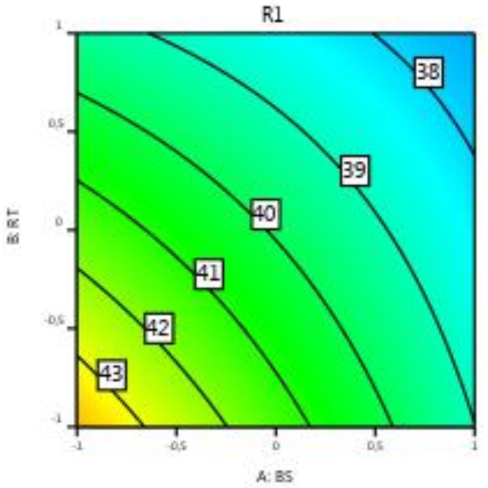
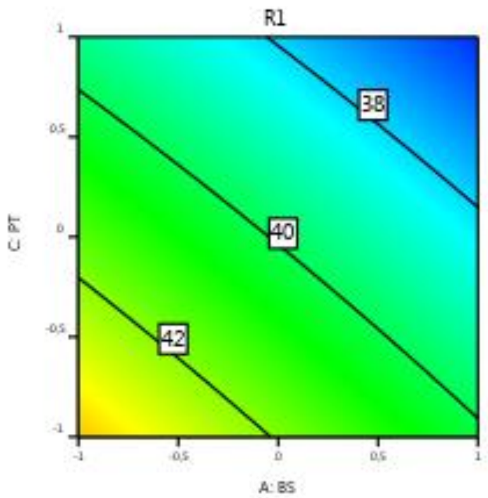
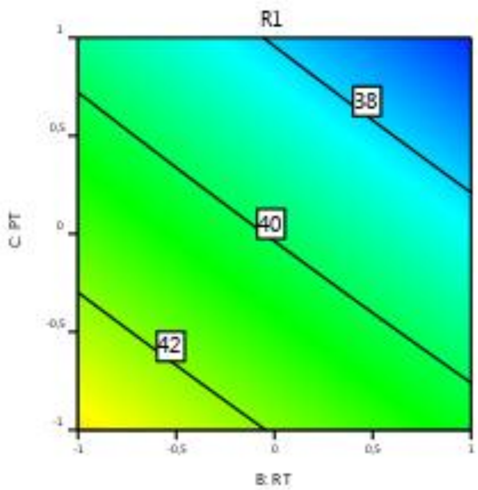
Biomass size vs Reactor temperature: *An adequate model was established for a yield of 39% when the biomass size was estimated to be less than 2mm and the reactor temperature was above 400°C.*	
Biomass size vs Pyrolysis reaction time: *An adequate model was established for a yield of 39% when the biomass size was estimated to be less than 2mm and the pyrolysis reaction time was greater than 2 hours.*	
Reactor temperature vs Pyrolysis reaction time: *An adequate model was established for a yield of 39% when the reactor temperature was above 400°C and the pyrolysis reaction time was greater than 2 hours.*	

Figure 1. Representation of 2D of the yield as a function of two factors.

3.2. Physicochemical characterization:

SEM analysis at a resolution of ×2000 (Figure 2) was conducted to examine the surface morphologies of all biochars derived from olive pomace. The obtained images revealed heterogeneous surfaces characterized by a highly porous structure, featuring cavities and varying pore sizes, including macropores, mesopores, and micropores **[17]**.

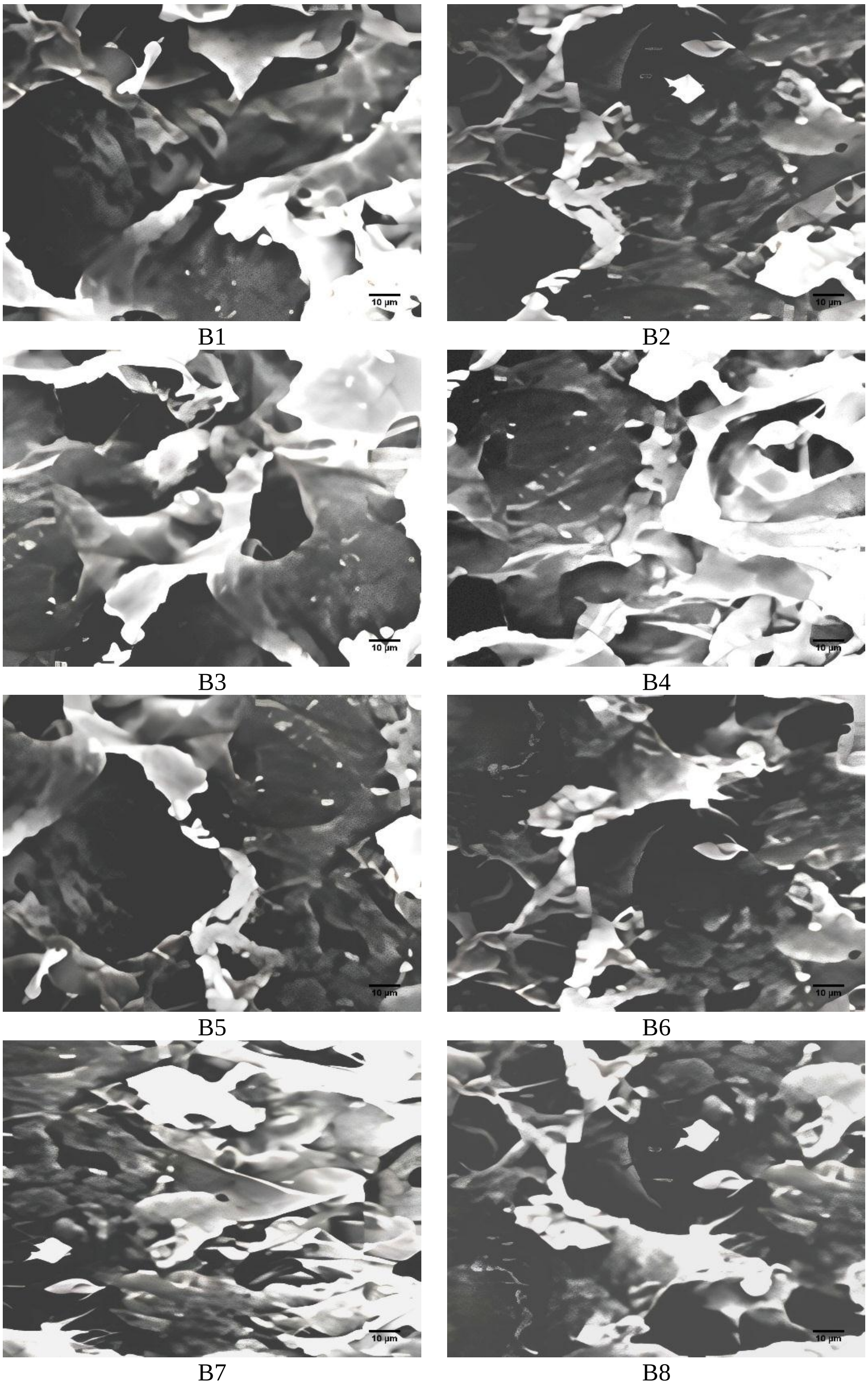


Figure 2. SEM of prepared biochars.

Micro-analysis using EDX (Table 4) provided insights into the elemental composition of the biochars. Notably, olive pomace biochar (OPB) exhibited a higher carbon percentage on its surface, ranging from 76.5% to 77.9%.

Table 4. composition of biochar samples according to EDX analysis.

Sample	C (%)	O (%)	Other Elements (%)
B1	76.5	22.1	1.4
B2	77.9	20.8	1.3
B3	77.4	21.4	1.2
B4	76.8	21.9	1.3
B5	77.2	21.3	1.5
B6	76.7	22.0	1.3
B7	76.9	21.5	1.6
B8	77.1	21.5	1.4

X-ray diffraction analysis was employed to investigate the atomic or molecular structure of the biochars (Figure 3). The diffraction patterns suggested a mainly amorphous nature for all biochars. The sharp peaks observed around 23° indicated the presence of a carbonaceous reticular plane resulting from the pyrolysis process. In contrast, the single crystalline phase in the diffraction pattern suggested that the biochars were predominantly composed of carbon **[18-19]**.

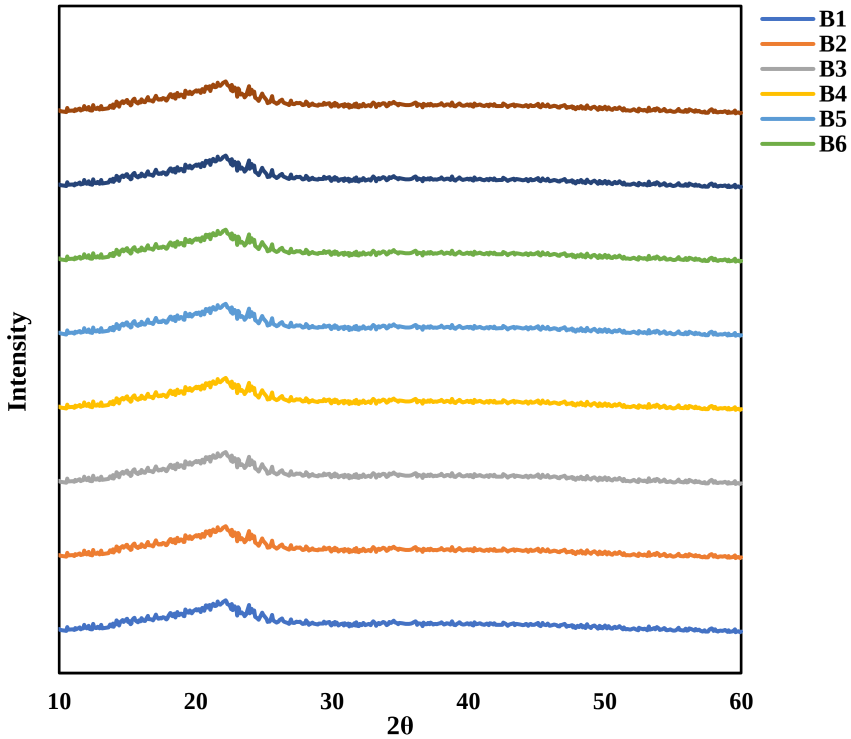


Figure 3. XRD of prepared biochars.

Surface and porosity properties of the biochar samples are presented in Table 5. Notably, all biochars exhibited significant adsorption properties, evidenced by higher pore volume (V_{Total}), higher pore surface area (S_{BET}), and smaller pore diameter (D_p).

Table 5. The specific surface area of biochar samples.

Sample	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	D_p (nm)
B1	13.4652	0.0212	3.2487
B2	13.0147	0.0211	3.3568
B3	13.5423	0.0221	3.6354
B4	13.5211	0.0222	3.3388
B5	13.2135	0.0214	3.4110
B6	13.1987	0.0208	3.3108
B7	13.0012	0.0208	3.1052
B8	12.9954	0.0201	3.0007

4. Discussion:

In recent years, there has been a significant increase in interest regarding pyrogenic carbon (C) in the form of biochar, which finds applications in agriculture, energy, medicine, and environmental sectors **[20]**. Biochar, a carbon-rich product distinct from charcoal and similar materials, is specifically produced for multiple applications **[21]**. For optimizing biochar production, having a comprehensive understanding of the chemical composition of biomass (cellulose or holocellulose - the total polysaccharide fraction, lignin, ash, and extractives) is crucial as the thermal degradation dynamics are highly dependent on it. Pyrolysis can be described as the direct thermal decomposition of an organic matrix, resulting in solid, liquid, and gas products **[22-24]**.

The primary objective of this research was to optimize the biochar production process using olive pomace waste with a pyrolysis process, employing a comprehensive 3-factor design of experiments with a Full Factorial Design model. The study focused on examining the individual effects of three crucial factors: biomass size, reactor temperature, and pyrolysis reaction time on biochar yield, using a 1st degree polynomial mathematical model. This study aimed to optimize the biochar elaboration process using a comprehensive design of experiments approach. Through analyzing the obtained results and developing a polynomial mathematical model, we gained valuable insights into the impact of key factors on biochar yield. The statistical parameters provide a robust evaluation of the model's performance and indicate areas for improvement. By fine-tuning the factors and controlling biomass size, reactor temperature, and pyrolysis reaction time, higher biochar yields and more sustainable production processes can be achieved. This research serves as a foundation for further investigations and advancements in the field of biochar production and its diverse applications, ultimately contributing to a more sustainable and eco-friendly future.

Furthermore, the elaborated biochars underwent extensive physicochemical analyses, including Scanning Electron Microscope coupled with Energy Dispersive X-Ray (SEM/EDX) and X-ray diffraction (XRD), and porosity parameters were determined using the Brunauer-Emmett-Teller method (BET). Stressing the importance of precise factor control, the research emphasized achieving higher biochar yields and promoting sustainability in production. Overall, this study provides valuable insights into biochar production, offering valuable guidance for future research to enhance its environmental applications.

The surface morphologies of biochars from olive pomace were analyzed using SEM at ×2000 resolution. The images displayed heterogeneous surfaces with a highly porous structure, including macropores, mesopores, and micropores. EDX analysis revealed that olive pomace biochar had a higher carbon percentage on its surface, ranging from 76.5% to 77.9%. X-ray diffraction (XRD) analysis showed that the biochars had a mainly amorphous nature with sharp peaks around 23°, indicating a carbonaceous reticular plane from the pyrolysis process. All biochars exhibited notable adsorption properties, as reflected by higher pore volume, surface area, and smaller pore diameter (Dp).

The growing interest in biochar's versatile applications necessitates an optimized production process. The research outlined in this study employed a comprehensive experimental design to identify key factors affecting biochar yield, offering insights to improve the production process and enhance its environmental applications. Additionally, the physicochemical characterization of the biochars highlights their unique properties and underscores their potential as sustainable alternatives for various sectors. By continuing to investigate and refine biochar production and utilization techniques, we can pave the way for a more sustainable and eco-friendly future, benefitting agriculture, energy, medicine, and the environment alike.

5. Conclusion:

In conclusion, this research focused on optimizing the biochar production process from olive pomace waste, utilizing a comprehensive 3-factor design of experiments with a Full Factorial Design model. The study explored the individual effects of key factors, namely biomass size, reactor temperature, and pyrolysis reaction time, on biochar yield using a 1st degree polynomial mathematical model. The findings clearly demonstrated the significant influence of these factors on the pyrolysis process, highlighting the importance of precise factor control for achieving higher biochar yields and promoting sustainable production practices. Moreover, thorough physicochemical analyses, including Scanning Electron Microscope coupled with Energy Dispersive X-Ray (SEM/EDX) and X-ray diffraction (XRD), were conducted to characterize the biochars derived from olive pomace. These analyses revealed highly porous surfaces with macropores, mesopores, and micropores, indicating their potential for diverse environmental applications, including soil amendment and water treatment. The study also revealed the predominantly amorphous nature of the biochars with a carbonaceous reticular plane, enhancing their adsorption capacity and catalytic activity. This property makes them efficient adsorbents for removing pollutants from soil and water. Overall, the research provides valuable insights into biochar production from olive pomace waste, offering guidance for future investigations to enhance environmental applications. The utilization of olive pomace for biochar production presents a sustainable solution for waste management and contributes to advancing the field of biochar technology for a greener and more sustainable future.

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