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# Operational parameters affecting synthesis yield and adsorption capacity of vine-pruning derived biochar for pesticide removal: Impact and modelling

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# ABSTRACT

This study optimizes  $CO_2$ -activated biochar production from vine shoots for adsorbing contaminants of emerging concern (CECs), focusing on pesticides acetamiprid, metalaxyl, and penconazole. Nine variables affecting biochar synthesis and adsorption capacity were examined using a two-step Design of Experiments (DOE). First, a Plackett–Burman Design screened five factors: biomass bed height, pyrolysis gas composition, pyrolysis gas flow, activation gas flow rate, and biomass particle size. Next, a Face-Centered Central Composite Design refined four key factors—pyrolysis temperature, pyrolysis time, activation temperature and activation time—to optimize both biochar synthesis yield and adsorption performance. Predictive models highlighted the importance of activation conditions in optimizing biochar's utility. Key physicochemical characterization confirmed the optimized biochar features. The best conditions, involving activation at 850 °C for 30 minutes, yielded biochar with a surface area of 740 m<sup>2</sup>/g, showing adsorption capacity of acetamiprid significantly surpasses reported efficiencies, with no comparable studies available for metalaxyl and penconazole. This research offers valuable insights into sustainable viticultural waste management, demonstrating the potential of vine-pruning biochar as an effective, eco-friendly adsorbent for CECs removal and laying groundwork for further environmental applications.

# 1. Introduction

Viticulture and winemaking constitute a significant sector in Europe, positioning it as the world's largest producer, consumer, and exporter of wine [1]. In 2022, there were 3.3 million hectares of vineyards across the continent, with Spain holding the distinction of having the largest area in both Europe and the world dedicated to this agricultural practice, covering 950,000 ha [2]. In Spain, over 2 million tons of vine shoots (VS) are generated annually during pruning. While the Waste and Contaminated Soils for a Circular Economy Act (Law 7/2022, dated April 8th) prioritizes biological treatment for compost production, small and micro-farms are permitted to incinerate these residues [3]. As a result, more than 1.2 million tons of VS were directly burned in the fields in 2019 [4].

The production of biochar offers an appealing method for valorising VS. Biochar, a solid material usually derived from the pyrolysis of biomass in an oxygen-limited environment [5,6], offers diverse environmental applications, like enhancing soil quality, energy production, and removal of contaminants of emerging concern (CECs) [7], like

pharmaceuticals, personal care products, industrial additives, microplastics, and pesticides [8,9]. Among all CECs, pesticides pose a significant challenge, because of their environmental relevance. For example, in 2015, the European Union added acetamiprid (ACE), an insecticide neonicotinoid, to its initial Watch List [10] due to potential risks. The third Watch List [11] introduced azole pesticides, including penconazole (PEN), which has been retained in the latest revision [12]. Also, metalaxyl (MET) is a fungicide with a high level of use around the world, especially in vineyards and greenhouses, and represents a threat to water quality [13].

Efficient removal of CECs in wastewater treatment plants (WWTPs) and drinking water treatment plants (DWTPs) require advanced technologies like ozonation, adsorption, membrane filtration, and advanced oxidation processes [14]. Among these, adsorption stands out as one of the most extensively employed technique due to its cost-effectiveness, high efficiency, and broad applicability [15], while biochar emerges as an innovative, economical, and environmentally friendly adsorbent material [16]. Biochar adsorption capacity can be significantly enhanced through physical or chemical activation processes. These aim

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to improve key properties involved in the adsorption operation, such as surface area, porosity, or the presence of functional groups [15]. Physical activation techniques, such as the use of  $CO_2$  at temperatures above 700 °C are especially appropriated. They can effectively improve the properties of biochar while offering a more environmentally friendly alternative to chemical methods, primarily due to the elimination of chemical reagents [17].

A comprehensive study of activated biochar production should consider numerous factors related to biomass pretreatment (i.e., particle size, ash and moisture content, chemical and biological pre-treatment) [18], pyrolysis (i.e., heating rate, maximum temperature, residence time, atmosphere composition or gas flow rate) [19] and activation (i.e., activation agent, maximum temperature, gas flow rate, pressure, and residence time) [20]. Rigorously studying all these variables is challenging due to their abundance and existing interactions among them. While many studies often use a traditional one-factor-at-a-time (OFAT) approach, employing a Design of Experiments methodology (DoE) is crucial. DoE allows the identification of significant factors and their higher-order terms (including interactions and quadratic terms) with fewer experiments, while also finding the real optimal synthesis conditions [21].

Previous research has explored VS derived biochar for applications in soil properties enhancement [22–24], soil remediation [25], energy production [26], and heavy metals adsorption in wastewater [27]. However, its effectiveness in adsorbing organic compounds, especially through a comprehensive DoE analysis, remains largely uncharted.

This study aims to evaluate the impact of several key factors on the synthesis yield and adsorption capacity of activated biochar derived from VS for three selected pesticides (ACE, MET and PEN). The relationship is modelled using a DoE approach. Initially, a Plackett-Burman Design (PBD) is used to assess the main effects of often overlooked variables such as pyrolysis gas composition, particle size, biomass bed height and gas flow rate. Then, a Face-Centered Central Composite Design (FCCD) is implemented, focused on four well-known key variables: pyrolysis time and temperature and activation time and temperature. The study is completed with the physicochemical characterization of the adsorbents produced to better understand these relationships. The creation of these models will provide a holistic understanding of the variables affecting both synthesis yield and adsorption capacity, helping underlying adsorption mechanisms and offering valuable insights and predictive tools for future biochar production as an adsorbent.

# 2. Material and methods

# 2.1. Chemicals and reagents

Acetamiprid (ACE, C<sub>10</sub>H<sub>11</sub>ClN<sub>4</sub>), Metalaxyl (MET, C<sub>15</sub>H<sub>21</sub>NO<sub>4</sub>), and Penconazole (PEN, C<sub>13</sub>H<sub>15</sub>C<sub>12</sub>N<sub>3</sub>) analytical standards were purchased from Sigma-Aldrich (Germany). Dipotassium hydrogen phosphate anhydrous (K<sub>2</sub>HPO<sub>4</sub>), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), orthophosphoric acid and acetonitrile were obtained from Panreac Química (Spain) and all were of analytical grade. Nitrogen gas (N<sub>2</sub> > 99.995), reductant gas (N<sub>2</sub>/H<sub>2</sub> 95:5 mixture), and carbon dioxide gas (CO<sub>2</sub> > 99.995) were supplied by Abelló Linde (Spain). Milli-Q water was produced using a water filtration system from Millipore (USA).

## 2.2. Plackett-Burman design

The Plackett-Burman Design (PBD) is a type of experimental design used primarily for efficiently screening multiple variables. It identifies the most significant factors affecting a process or outcome by testing multiple variables simultaneously while reducing the number of experimental runs. PBD is particularly useful in preliminary experiments, focusing on the main effects and assuming that interactions between factors are negligible. In this study, PBD was employed to determine whether the following variables significantly influence the synthesis of activated biochar: initial biomass bed height and particle size, pyrolysis gas flow and composition, and activation gas flow. Each variable was tested at two distinct levels, coded as -1 and +1. In this context, a 'level' refers to the specific value or condition that a factor can take within an experiment. A level of -1 indicates the lower condition or value of the variable, while a level of +1 indicates the higher condition or value. To examine the effects of the five factors, the PBD required eight experiments. Furthermore, three experiments were replicated to estimate the variability of the synthesis process. A further explanation of the methodology used can be found elsewhere [21].

The response variables selected for this study include the activated biochar synthesis yield (denoted as Y, measured in % and calculated as the final, dry activated biochar obtained divided by the initial, dry biomass) and the adsorption capacities at equilibrium (represented as  $q_e$ , in mg of micropollutant adsorbed per g of biochar) for ACE, MET, and PEN. ACE, MET and PEN were selected because are uncharged at pH 7 and showcase diverse molecular hydrophobicity levels (log K<sub>ow</sub> = 0.8, 1.65 and 3.72 for ACE, MET and PEN respectively) [28–30]. Table 1 provides an overview of the chosen levels for each factor examined in the current PBD.

# 2.3. Face-centered central composite design

A FCCD is a type of experimental design used in response surface methodology, where the star points are positioned at the center of each face of the factorial space. This design is primarily used for modelling curvature in the response surface, which helps in understanding the relationship between factors and the response variable. It is particularly useful for optimizing processes and finding the best operating conditions. In this study, a comprehensive exploration of four key variables – temperature and time of pyrolysis and temperature and time of activation- was conducted using a FCCD. The FCCD integrates a factorial design at two levels with a star design and n center points, assigning three coded levels (-1, 0, +1) to each factor. For a four-factor FCCD, a total of 27 runs are required: 16 for the factorial design, 8 for the star design, and 3 for the center points. This approach allows the estimation of the coefficients ( $b_{xy}$ ...) of the following model:

$$RV = b_0 + b_1X_1 + \dots + b_4X_4 + b_{12}X_1X_2 + \dots + b_{34}X_3X_4 + b_{11}X_1^2 + \dots + b_{44}X_4^2$$
(1)

where RV is the response variable and  $X_i$  refers to the studied factors. The response variables selected are the same ones of the PBD (the activated biochar synthesis yield (Y), and the adsorption capacity at equilibrium (q<sub>e</sub>) of ACE, MET and PEN). Table 2 details the selected levels for each factor that are being examined in the present FCCD. For better understanding of the FCCD approach, it has been applied following the methodology described by Leardi (2013) [21].

# 2.4. Software

The CAT software (Chemometric Agile Tool, version of September 5, 2023) was employed for processing the data obtained from the experimental designs. CAT is an R-based chemometric tool, and it can be freely downloaded from http://gruppochemiometria.it/index.php/software.

Table	1
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Experimental ranges for the factors in the Plackett-Burman experimental design.

Code	Factors	Levels Low (-1)	High (+1)
X <sub>1</sub>	Biomass bed height (mm)	5	10
X <sub>2</sub>	Pyrolysis gas composition	99.995 % N <sub>2</sub>	N <sub>2</sub> /H <sub>2</sub> 95:5 mixture
X <sub>3</sub>	Pyrolysis gas flow (L min <sup>-1</sup> )	2	6
X <sub>4</sub>	Biomass particle size (µm)	125	250
X <sub>5</sub>	Activation gas flow (L min <sup>-1</sup> )	2	6

#### Table 2

Experimental ranges for the studied factors in the face-centered central composite design (FCCD).

Code	Factors	Levels Low (-1)	Central (0)	High (+1)
X <sub>6</sub>	Pyrolysis temperature (°C)	350	500	650
X7	Pyrolysis time (h)	1.5	3	4.5
X <sub>8</sub>	Activation temperature (°C)	700	775	850
X9	Activation time (min)	10	20	30

# 2.4.1. Biomass material preparation

Vineyard shoots (VS) were chosen as feedstock for activated biochar production. VS were provided by the LIFE project VINEYARDS4HEAT (LIFE13 ENV/ES000776), which obtained it from vineyard pruning conducted in January 2021 in the Alt Penedès region of Catalunya, northeastern Spain. The *Vitis vinifera* plant shoots were cleaned with Milli-Q water to remove dust and dirt and subsequently air-dried at room temperature. The shoots were manually cut to 0.5 cm in size and further oven-dried at 70 °C for 48 hours. The drying was followed by a milling process using a RETSCH RS100 ring mill at a speed of 1400 rpm for 8 seconds. After the VS were crushed, they were sieved, resulting in two distinct particle size fractions: one fraction with sizes between 500 and 250  $\mu$ m, and the second consisted of particles between 250 and 125  $\mu$ m. For the purposes of this study, these fractions are referred to as the 250  $\mu$ m and 125  $\mu$ m particle sizes, respectively.

# 2.4.2. Pyrolysis and activation steps

A specific quantity of sieved VS (particle size 125 or 250 µm, depending on the PBD level, and fixed at 250 µm in the FCCD) was dried again at 70 °C until a constant weight and introduced into two ceramic crucibles (each with 7 or 14 g of VS, to reach 5 or 10 mm of biomass height depending on the PBD level, or fixed at 10 g in the FCCD). These two crucibles were placed in a protective box and heated using a muffle furnace N11/HR from Nabertherm (Germany) with a heating rate of 10 °C min<sup>-1</sup>. The biochar synthesis started with a pyrolysis phase at a stable temperature of 500 °C for 4 hours in the PBD, while in the FCCD, both the temperature and time of pyrolysis varied according to the experimental level. An oxygen-free environment was maintained by introducing a flow of pure nitrogen or a nitrogen-hydrogen mix (as determined by the PBD level). In the FCCD experiments, exclusively pure nitrogen was feed into the protective box. Once pyrolysis finished, the VS biochar underwent physical activation with CO<sub>2</sub> gas in a consecutive stage, heating the material to an activation temperature of 800 °C for 1 hour in the PBD, with the FCCD employing variable activation temperatures and times based on the specific level. The gas flow rate during both stages was set at either 2 or 6 L min<sup>-1</sup> in the PBD and fixed at 4 L min<sup>-1</sup> in the FCCD.

# 2.5. Physicochemical characterization techniques

The ash content of the materials was determined in accordance with the ISO 18122:2022 procedure. Thermogravimetric analysis (TGA) was carried out using an SDT Q600 analyser from TA Instruments (USA), equipped with a XP5U balance and operated under a nitrogen flow rate of 60 mL min<sup>-1</sup>. The temperature ramped up to 1000 °C with a heating rate of 10 °C min<sup>-1</sup>. The initial weight of the VS samples before heating was approximately 10 mg.

To analyse the functional groups, present on the material's surface, Fourier Transform Infrared (FTIR) Spectra were obtained using the Spectrum Two<sup>TM</sup> FTIR spectrometer from PerkinElmer (USA). Multiple scans were performed across wavenumbers ranging from 450 to  $4000 \text{ cm}^{-1}$ , at a resolution of  $4 \text{ cm}^{-1}$ . The surface morphology and structural characteristics were examined using the FESEM JSM-7100-F from JEOL (Japan), which operated at an acceleration voltage of 20 kV. The samples were carbon-coated prior to this analysis, with a 208 C coater from Cressington (UK). The BET (Brunauer, Emmett, and Teller) surface area (S<sub>BET</sub>) and pore size distribution were assessed using N<sub>2</sub> adsorption and desorption isotherms via a TriStar 3000 from Micrometrics (USA). Between 0.1 g and 1 g of each sample was subjected to a degassing process at 100 °C for 12 hours to eliminate any residual moisture and volatile substances before conducting the measurements. Micropores were characterized as having a diameter < 2 nm, mesopores ranged from 2 to 50 nm, and macropores exceeded 50 nm, following the classification recommended by IUPAC [31].

The content of carbon (C), hydrogen (H), and nitrogen (N) in the samples was analysed using an EA 3100 elemental analyser from Eurovector (Italy). Samples weighing 1000–2000  $\mu$ g were measured using a microbalance WXTS3DU from Mettler Toledo (Switzerland). The analysis of C, H, and N involved combustion under standard conditions (carrier gas pressure 90 kPa, reactor temperature 980 °C, column temperature 90 °C), with vanadium pentoxide as a combustion aid. The oxygen (O) content was determined using the same analyser, but through pyrolysis under recommended standard conditions (carrier gas pressure 80 kPa, reactor temperature 1000 °C, column temperature 100 °C).

The biochemical fractionation of the 250  $\mu$ m VS fraction was conducted by the Forest Science and Technology Centre of Catalonia (CTFC) following a modified Klason lignin method [32]. First, 300 mg of dry, finely ground material was extracted with ethanol:benzene (1:1, v/v) at 60 °C for 1 hour, centrifuged, and the process repeated twice. The extracts were concentrated for dry weight lipid determination. The remaining pellet was hydrolysed with 1 N sulfuric acid at 110 °C for 1 hour, followed by centrifugation and sugar analysis using the phenol-sulfuric acid method [33], representing the non-cellulosic polysaccharide fraction. The dried pellet was then treated with 72 % sulfuric acid at room temperature for 4 hours, diluted, boiled, and filtered. The hydrolysate was analysed for sugars to determine the cellulose fraction, while the solid residue was dried and weighed, with the loss on ignition considered the lignin fraction.

# 2.6. Adsorption capacity tests

The adsorption capacity of ACE, MET, and PEN at equilibrium, used as the response variable in the PBD and FCCD, was determined through batch experiments. For this purpose, 12.5 mg of biochar was added to a 250 mL solution containing 0.08 mmol L<sup>-1</sup> of each pollutant. The pH of these solutions was adjusted to 7.0  $\pm$  0.1 using a 5 mmol L<sup>-1</sup> K<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub> buffer. These solutions were prepared by diluting stock solutions of 300 mg L<sup>-1</sup> of ACE, 300 mg L<sup>-1</sup> of MET, and 50 mg L<sup>-1</sup> of PEN in Milli-Q water.

When biochar was added to the solution, the experiments were stirred at 280 rpm on a multi-platform orbital Shaker from Fisherbrand (USA) for 72 hours until equilibrium was reached, maintaining a temperature of 25 °C. The initial and equilibrium concentrations of micropollutants were measured in triplicate. For each sampling, 1 mL of the solution was extracted using a syringe and filtered through a 0.45- µm PVDF filter. The filtered samples were then analysed by High-Performance Liquid Chromatography (HPLC). The HPLC analyses were performed using a 1260 Infinity Series system from Agilent Technologies (USA), equipped with a SEA18 Teknokroma column (250  $\times$  4.6 mm i.d.; 5 µm particle size). For the mobile phases, acetonitrile and water acidified to pH 3 with orthophosphoric acid were used. An isocratic method was employed with a flow rate set at 1 mL min<sup>-1</sup>. The injection volumes for ACE, MET, and PEN were 10, 26, and 18 µL, respectively. The acetonitrile:water ratio in the mobile phase was adjusted to 40:60 for ACE, 60:40 for MET, and 70:30 for PEN. Detection wavelengths were set at 250 nm for ACE and 220 nm for both MET and PEN.

The adsorption capacity at equilibrium ( $q_e$  in mg g<sup>-1</sup>) for ACE, MET, and PEN was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

Where  $C_0 \text{ (mg } L^{-1})$  represents the initial micropollutant concentration,  $C_e \text{ (mg } L^{-1})$  is the micropollutant concentration at equilibrium, V (L) is the volume of the solution and m (g) is the mass of the used biochar.

# 3. Results and discussion

Nine variables were selected for their potential impact on the synthesis process of activated biochar. In experimental design, these variables are referred to as 'factors'. This study focused on four of them—temperature and time of pyrolysis, and temperature and time of activation— identified as critical based on preliminary tests and bibliographic review [17,20,34]. These factors were exhaustively evaluated through FCCD. The remaining variables, which are important but less frequently studied, include initial biomass bed height and particle size, pyrolysis gas flow and composition, and activation gas flow. These variables were assessed through a screening study using a PBD. The selected methodologies enable the identification of the relevant factors under study, with a minimal number of experimental runs.

# 3.1. Plackett-Burman experimental design

As summarized in Table 1, the gas flow for pyrolysis and activation was adjusted to 2 and 6 L min<sup>-1</sup> to study a range, including the oven manufacturer's recommended minimum of 5 L min<sup>-1</sup>, to assess the potential for reducing gas consumption without compromising process efficiency. The effect of biomass height in ceramic crucibles on pyrolysis and activation processes was investigated by filling them to maximum (14 g each to reach 10 mm of biomass height) and half capacity (7 g each to reach 5 mm of biomass height). This study was particularly important due to the tangential gas flow over the biomass in our setup, causing differential gas diffusion. During the activation phase, a concentration gradient of  $CO_2$  in the biomass bed is expected, affecting the reaction based on the biomass load.

Two protective atmospheres were studied in the pyrolysis process: an inert atmosphere with pure nitrogen, and a reducing atmosphere with 95 % N<sub>2</sub> and 5 % H<sub>2</sub>, as these influence biochar properties [35]. Furthermore, considering the impact of particle size on activated biochar adsorption capacity [36], two particle sizes – 125 and 250  $\mu$ m – were selected for this design. ACE, MET and PEN adsorption capacities were selected as response variables based on their pKa and K<sub>OW</sub>. These compounds are uncharged at pH 7 and exhibit varying levels of molecular hydrophobicity, with log K<sub>ow</sub> values of 0.8, 1.65 and 3.72 for ACE, MET and PEN respectively [28–30].

The PBD matrix, detailing the conditions of each experimental run and the corresponding results for the measured response variables, is provided in Table S1 from the supplementary material.

The coefficients for the factors assessed in the PBD, shown in Fig. 1



**Fig. 1.** Plot of the coefficients of the model obtained by the Plackett-Burman design (the green bracket indicates the confidence interval at p = 0.05; \* = p < 0.05, \*\* = p < 0.01; \*\*\* = p < 0.001). For detailed identification of which factors correspond to X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, and X<sub>5</sub>, refer to Table 1.

and detailed in Table S2 from the supplementary material, reveal that factor  $X_1$  (biomass height in each ceramic crucible) is the most significant. This factor has a statistically significant impact (p < 0.01) on each response variable. Specifically, a positive coefficient for factor  $X_1$  implies that a higher biomass height increases the yield of activated biochar production. On the other side, when it comes to the adsorption capacity for ACE, MET, and PEN, the negative coefficient associated with factor  $X_1$  indicates that an increased biomass height leads to a reduced adsorption capacity for the produced biochar. This increase in yield and reduction in the adsorption capacity at higher bed heights can be attributed to poor  $CO_2$  diffusion through the biomass, leading to incomplete activation of the inferior layers.

Factor  $X_5$  (CO<sub>2</sub> flow rate during activation) is statistically significant for  $q_{e\ MET}$ , as a higher CO<sub>2</sub> flow enhances the concentration gradient, improving oxidant diffusion into the pores and thus activation [20]. The  $q_{e\ MET}$  model also revealed statistical significance of factor  $X_2$ (p < 0.05). Therefore, MET adsorption is best achieved by employing a reducing gas as protective atmosphere during pyrolysis. Santos et al. [35] observed that reductant atmospheres, especially a 1:1 N<sub>2</sub>/H<sub>2</sub> mixture, can modify the physicochemical properties of biochar during pyrolysis. Nevertheless, compared to the effect of factor  $X_1$ , the impact of factors  $X_2$  and  $X_5$  on the response variable can be considered negligible.

Based on the evaluation of the PBD results, all the studied factors were fixed for the subsequent FCCD study. For biomass height (factor  $X_1$ ), an intermediate level of 10 g per ceramic was selected. This choice aimed to balance between achieving high adsorption capacity and optimizing synthesis yield. The flow rates for pyrolysis and activation (factors  $X_3$  and  $X_5$ ) were set at 4 L min<sup>-1</sup>. Although the use of a reducing gas was found to enhance the  $q_{e MET}$  in the produced activated biochar, its limited effect on this specific response variable led to the selection of nitrogen as the pyrolysis gas (factor  $X_2$ ), primarily due to its cost-effectiveness. A particle size of 250 µm for the biomass (factor  $X_4$ ) was chosen, as it is the predominant size produced in the grinding and sieving process.

# 3.2. Face-centered central composite design

The FCCD was proposed to investigate the main factors affecting yield and adsorption capacity of biochar: temperature and time of pyrolysis and temperature and time of activation stage. FCCD incorporates constant and linear terms, as well as interactions between factor pairs and quadratic terms, which determines the curvature of the response surface.

Pyrolysis and activation temperature and time were studied according to levels detailed in Table 2. The chosen range for pyrolysis temperature (factor X<sub>6</sub>) was based on the composition of VS, which have a complex matrix of cellulose (32-40 %), hemicellulose (5-27 %), and lignin (16-39 %) [37]. Specifically, for the 250 µm fraction of VS used as biomass feedstock, the composition was 26.62  $\pm$  0.08 % non-cellulosic polysaccharides, 21.99  $\pm$  0.50 % cellulose, and 18.17  $\pm$  0.40 % lignin. Lignin resist thermal degradation (160 up to 900 °C), while cellulose and hemicelluloses decompose at lower temperatures (315-400 °C and 220-315 °C respectively) [18,38]. TGA results showed major weight loss in VS between 200 and 350 °C due to hemicellulose and cellulose decomposition, and gradual loss thereafter due to cellulose and lignin breakdown, as detailed in the figure S1 from the supplementary material. Based on these observations, the range for the pyrolysis temperature (factor X6) was set between 350 and 650 °C. Pyrolysis time (factor X<sub>7</sub>) ranged from 1.5 to 4.5 hours based on bibliographic data [17,39].

Regarding activation,  $CO_2$  induces pore formation in biochar by selectively removing carbon atoms, as described by the endothermic Boudouard reaction (Eq. (3)), which requires 159 kJ mol<sup>-1</sup> of heat.

$$CO_2 \rightarrow 2CO$$

This endothermic process allows controlled biochar transformation

(3)

C +

by regulating heat and residence time [40]. Literature suggests a minimum activation temperature of 700 °C due to the high heat needed to favour CO production [20]. The upper limit, set at 850 °C, prevents the formation of carbon-free structure consisting mostly of ashes. Optimal activation time, determined also from those preliminary studies, falls between 10 and 30 minutes to avoid complete oxidation during longer residence in the activation phase.

The FCCD matrix, detailing the conditions for each run and the corresponding results for the response variables, is provided in Table S3 from the supplementary material.

Fig. 2 illustrates the relationship between yield and adsorption capacity, with the Y-axis showing the ACE adsorption capacity (log(qe ACE)) and the X-axis showing the synthesis yield. Similar trends for MET and PEN are detailed in Figures S2 and S3 from the supplementary material. The figure highlights the need to balance both variables, since there is an inverse correlation: higher adsorption capacity of pesticide in the biochar results in lower synthesis yield.

# 3.2.1. Evaluation of the synthesis yield (Y, %)

Based on the FCCD results detailed in Table S3 from the supplementary material, a multivariate regression was performed on this data to obtain a mathematical expression that describes biochar yield (Y) as a function of temperature and time during pyrolysis ( $X_6$ ,  $X_7$ ) and temperature and time during activation ( $X_8$ ,  $X_9$ ). Eq. (4) shows the corresponding model with significant coefficients, which are represented in Fig. 3.

$$\begin{split} Y =& 24.32 - 0.80 X_6(***) - 0.51 X_7(***) - 4.81 X_8(***) \\ &- 2.46 X_9(***) - 0.42 X_6 X_7(**) - 0.073 X_6 X_8 + 0.04 X_6 X_9 \\ &- 0.09 X_7 X_8 - 0.15 X_7 X_9 - 1.70 X_8 X_9(***) - 0.162 X_6^2 - 0.20 X_7^2 \\ &- 1.18 X_8^2(**) + 0.38 X_9^2 \end{split}$$

The asterisks in the equation denote the significance level of each coefficient, with lower p-values denoting higher influence (\* = p < 0.05, \*\* = p < 0.01; \*\*\* = p < 0.001). The adjusted R<sup>2</sup> is 0.99, and the standard deviation of the residuals is 0.47.



**Fig. 2.** Scatter plot of the variables biochar synthesis yield (X-axis) and biochar log (q<sub>e ACE</sub>) (Y-axis) across the 27 experimental runs from the FCCD. The numbers depicted correspond to the experimental runs as detailed in Table S3 from the supplementary material.

# Coefficients synthesis yield (Y, %)



**Fig. 3.** Plot of the coefficients (Eq. (4)) of the model for biochar yield obtained by the FCCD (the green bracket indicates the confidence interval at p = 0.05; \* = p < 0.05, \*\* = p < 0.01; \*\*\* = p < 0.001). Factors  $X_6$  and  $X_7$  refer to pyrolysis temperature and time, respectively, while factors  $X_8$  and  $X_9$  correspond to activation temperature and time.

According to Fig. 3, the significant coefficients include all linear terms ( $X_6$ ,  $X_7$ ,  $X_8$ ,  $X_9$ ), the interaction terms  $X_6X_7$  and  $X_8X_9$ , and the quadratic term for  $X_8$ . This indicates that each factor significantly impacts the response variable. Particularly, the terms associated with the activation step ( $X_8$  and  $X_9$ ) emerge as the most influential in the model.

The negative coefficients for the linear terms for  $X_6$ ,  $X_7$ ,  $X_8$  and  $X_9$  indicate that increasing these factors individually decreases synthesis yield. This suggests that lower temperatures and shorter times during pyrolysis and activation stages are preferred for higher yield. TGA results indicate that lower pyrolysis conditions (350 °C, 1.5 hours) lead to higher synthesis yield due to incomplete decomposition of VS components, while higher conditions (650 °C, 4.5 hours) reduce yield, leaving mostly thermal-resistant lignin. In line with these results, Adilah et al. [41] noted that biochar production increases with higher lignin content in feedstock.

Due to the significant and large higher terms (interaction and quadratic terms) involved in the activation factors, a response surface has been generated to deeper evaluate the phenomenon. In Fig. 4, the effect of activation factors  $X_8$  and  $X_9$  can be studied while the pyrolysis factors  $X_6$  and  $X_7$  are kept fixed at their central or neutral level (+0) to isolate the impact of the activation factors.

The X<sub>8</sub>- X<sub>9</sub> plane response surface reveals that activation time primarily affects yield at high temperatures. Optimal yields are obtained at 700 °C, regardless of activation time. Literature asserts that temperatures above 700 °C are required for the Boudouard reaction to selectively remove carbon from biochar. At 700 °C, VS are less reactive with CO<sub>2</sub> than at higher temperatures [42]. Therefore, extending activation time from 10 to 30 minutes does not significantly impact yield at 700 °C. Near 850 °C, the biomass gasification reaction rate increases, leading to fastest carbon removal and reduced yield. Prolonging the activation time at high temperatures causes over-activation, removing carbon until only ashes remain [20].

# 3.2.2. Evaluation of ACE, MET and PEN adsorption capacity $(q_e)$

Eqs. (5), (6), and (7) models the relationship between the logarithm of the adsorption capacities of ACE, MET, and PEN, respectively, and the

# Contour Plot synthesis yield (Y, %)



**Fig. 4.** Response surface of the Yield (%) on the plane  $X_8$ - $X_9$  (activation temperature vs activation time).  $X_6$  and  $X_7$  fixed at level 0 (pyrolysis temperature and pyrolysis time).

factors under study (see Table 2). The adjusted  $R^2$  values are 0.98, 0.96, and 0.89, with the standard deviation of the residuals being 0.07, 0.11, and 0.05 for the ACE, MET, and PEN models, respectively. The estimated coefficients for these models are represented in Fig. 5.

$$\log(q_{eACE}) = 1.29 + 0.06X_6(**) + 0.03X_7 + 0.04X_8(***)$$

$$+0.29X_9(***)+0.03X_6X_7-0.04X_6X_8(*)-0.03X_6X_9(*)$$

$$-0.00X_7X_8 - 0.03X_7X_9 + 0.12X_8X_9(***) - 0.01X_6^2$$

$$\begin{split} \log(q_{eACE}) &= 1.29 + 0.06 X_6(**) + 0.03 X_7 + 0.04 X_8(***) \\ &+ 0.29 X_9(***) + 0.03 X_6 X_7 - 0.04 X_6 X_8(*) - 0.03 X_6 X_9(*) \\ &- 0.00 X_7 X_8 - 0.03 X_7 X_9 + 0.12 X_8 X_9(***) - 0.01 X_6^2 \\ &- 0.08 X_7^2 + 0.22 X_8^2(***) - 0.01 X_9^2 \end{split}$$

$$log(q_{ePEN}) = 1.93 - 0.03X_{6}(*) + 0.01X_{7} + 0.08X_{8}(***) + 0.10X_{9}(***) + 0.00X_{6}X_{7} + 0.00X_{6}X_{8} - 0.00X_{6}X_{9} + 0.02X_{7}X_{8} + 0.01X_{7}X_{9} + 0.09X_{8}X_{9}(***) + 0.03X_{6}^{2} + 0.07X_{7}^{2} + 0.01X_{8}^{2} + 0.01X_{9}^{2}$$
(7)

Activation temperature (X<sub>8</sub>) and time (X<sub>9</sub>) are the most influential factors for the adsorption capacity in ACE, MET, and PEN models, exhibiting the largest linear effects and a notable interaction (X<sub>8</sub>X<sub>9</sub>). Fig. 6 shows the response surface of the log (ACE, MET, and PEN q<sub>e</sub>) on the X<sub>8</sub>-X<sub>9</sub> plane (activation temperature vs. activation time). As it can be observed, optimal adsorption occurs at 850 °C for 30 minutes. However, at 700 °C, longer activation times barely affect adsorption capacity, as discussed in more detail in Section 3.3 of the physicochemical characterization of the biochar.

Although less impactful, pyrolysis temperature (X<sub>6</sub>) is also

statistically significant in all models, being positive for ACE and MET. This suggests that higher pyrolysis temperatures (650  $^{\circ}$ C) enhance the adsorption capacity of the produced activated biochar. On the contrary, in the PEN model, this coefficient is negative, indicating that higher pyrolysis temperatures reduce the adsorption capacity of PEN in the biochar. These observations will be further analysed in Section 3.3 of the physicochemical characterization of the biochar.

Pyrolysis time ( $X_7$ ;1.5–4.5 hours) does not significantly impact the adsorption capacity of ACE or PEN, and only slightly affects MET adsorption, with longer times (4.5 hours) being more effective. However, this effect is almost negligible in front of activation factors. Given the limited influence of pyrolysis time on biochar adsorption capacity for these compounds, future studies should consider shorter pyrolysis times (below 1.5 hours) to optimize the process, save energy, and reduce N<sub>2</sub> consumption.

The ACE model shows that, while the interaction between activation factors (X<sub>8</sub>X<sub>9</sub>) has the greatest impact on response variables, the interactions between pyrolysis temperature and activation temperature  $(X_6X_8)$ , as well as activation time  $(X_6X_9)$ , are also statistically significant. Although the linear terms of these factors individually have positive coefficients, their interactions show negative coefficients. This indicates that while each factor increase independently improves adsorption capacity, their simultaneous increase produces a less beneficial combined effect. As further discussed in the biochar characterization, higher pyrolysis temperatures (650 °C) increase porosity, which is key for ACE adsorption. However, when biochar with enhanced pyrolysis porosity undergoes high activation temperature (X<sub>8</sub>) and activation time (X<sub>9</sub>), the interaction with CO2 and carbon adsorbents, particularly in micropores, can lead to micropore enlargement or collapse, reducing total surface area and adsorption capacity [20]. These results underscore the importance of considering both individual and combined effects in biochar production and highlight the complexity of the underlying chemical and physical processes. The FCCD provides a strong approach to understanding these complex, non-linear interactions.

# 3.2.3. Physicochemical characterization of the VS biomass and biochar

To gain a deeper understanding of the variables influencing both synthesis and adsorption capacity, physicochemical characterization was conducted on 8 of the 27 materials synthesized for the FCCD, as shown in Table 3: those of highest adsorption capacities (runs 4, 8, 12, 16), one biochar with the lowest adsorption performance (run 1), and two materials synthesized at medium levels (runs 22 and 26). Finally, to assess the impact of pyrolysis on the produced biochar, run 13 was also characterized. To further study the impact of pyrolysis and activations stages on the final adsorption capacity, two best-performing materials (run 4 and run 16) were synthesized skipping the activation stage (named 4 NA and 16 NA, respectively). Furthermore, to specifically evaluate the role of  $CO_2$  in the activation process, two additional materials were synthesized using N<sub>2</sub> instead of  $CO_2$  during activation, while maintaining the pyrolysis conditions of runs 4 and 16 (named 4 NCO<sub>2</sub> and 16 NCO<sub>2</sub>, respectively).

Higher surface areas imply a more extensive network of pores and surface sites available for adsorption, as confirmed by the current results. The pristine VS, with a  $S_{BET}$  of 0.68 m<sup>2</sup> g<sup>-1</sup>, showed no adsorption capacity for ACE and MET (0.5 and 0.0 mg g<sup>-1</sup>, respectively), and only moderate adsorption for PEN (19.7 mg g<sup>-1</sup>). Run 1, conducted at the lowest factor levels, produced the highest yield (29.57 %) but had a low  $S_{BET}$  (4.4 m<sup>2</sup> g<sup>-1</sup>) and minimal adsorption for ACE and MET (1.4, 4.4 mg g<sup>-1</sup> respectively). These values were not significantly different from the results obtained with raw biomass. Only PEN adsorption was enhanced up to 103 mg g<sup>-1</sup>.

Improved adsorption capacities for all pesticides were achieved under the conditions of runs 4, 8, 12, and 16, characterized by elevated temperatures and long activation times. Accordingly, the FCCD revealed a notable linear impact and a strong interaction of both activation factors ( $X_8$  and  $X_9$ ) in the ACE, MET, and PEN models (Eqs. (5), (6), (7)).

8\*X9 X6^2 X7^2 X8^2 X9^2



## Coefficients log (PEN Qe)



**Fig. 5.** Plot of the coefficients for the logarithmic  $q_e$  of ACE (Eq. (5)), MET (Eq. (6)), and PEN (Eq. (7)), obtained from the FCCD (the green bracket indicates the confidence interval at p = 0.05; \* = p < 0.05; \*\* = p < 0.01; \*\*\* = p < 0.001). Factors  $X_6$  and  $X_7$  refer to pyrolysis temperature and time, respectively, while factors  $X_8$  and  $X_9$  correspond to activation temperature and time.

This scenario led to a notable increase in  $S_{BET}$ , peaking at 740.36 m<sup>2</sup> g<sup>-1</sup> in run 4. Consequently, adsorption capacities for ACE, MET, and PEN increased to 171.7, 91.9, and 209.5 mg g<sup>-1</sup> respectively, correlating with a decreased yield to 15.65 %. Table 4 presents all the adsorption studies found for MET and PEN in ultrapure water and single-component systems, along with the most recent research on ACE. These findings demonstrate the significant potential of vine-pruning-derived activated biochar as an adsorbent, given its remarkable adsorption capacities in comparison with other adsorbent materials. Significantly, the adsorption capacity of ACE on vine-pruning-derived biochar (171.7 mg g<sup>-1</sup>) surpasses that of reported commercial activated carbon (163.7 mg g<sup>-1</sup>).

The enhanced porosity observed in runs 4, 8, 12 and 16 is primarily due to the Boudouard reaction, where  $CO_2$  selectively removes carbon atoms [20]. However, it is not the only mechanism for increasing surface area. For example, material 4 NCO<sub>2</sub>, synthesized using N<sub>2</sub> instead of  $CO_2$ during activation, the surface area was only 6.56 m<sup>2</sup> g<sup>-1</sup>. In contrast, material 16 NCO<sub>2</sub>, synthetized under similar  $CO_2$ -free conditions but at higher pyrolysis temperature, exhibited a notable increase in surface area to 74.62 m<sup>2</sup> g<sup>-1</sup>. These results align with the positive coefficient of pyrolysis temperature (X<sub>6</sub>) in the ACE and MET models (Eqs. (5), (6)). Previous research suggests that increasing pyrolysis temperatures enhances material porosity by thermally fracturing pore-blocking substances [50], decomposing organic components like cellulose and lignin [51], which forms vascular bundles or channel structures, and releasing volatile matter [52].

Despite the direct correlation between PEN adsorption and S<sub>BET</sub>, FCCD model displays a X<sub>6</sub> (pyrolysis temperature) negative coefficient. Moreover, significant removal also occurs in less porous materials like run 1, unlike ACE and MET, which are not adsorbed. This means that other mechanisms could contribute to PEN sorption. Literature shows that the sorption of neutral and hydrophobic organic molecules, such as PEN, may be driven by hydrophobic interactions and the partitioning process [53]. For example, Chen et al. [54] found that at lower pyrolysis temperatures (100-300 °C, close to pyrolysis conditions for run 1), partitioning was the predominant sorption mechanism for organic pollutants in non-carbonized biochar fractions. Conversely, at higher temperatures (400-700 °C), adsorption onto porous carbonized fractions becomes more dominant, creating a mixed adsorption-partition system. Additionally, Rodríguez-Cruz et al. [55] examined the sorption of MET and PEN by organo-clays, highlighting the significant role of the partitioning process in the organic phase for PEN compared to MET. These results would suggest that materials synthesized at lower pyrolysis temperatures, which may contain partially carbonized biochar fractions, can still exhibit significant capabilities for hydrophobic pesticide removal. Therefore, in this mixed adsorption-partitioning system, although a high level in the pyrolysis temperature factor should promote



Contour Plot log (PEN Qe)



Fig. 6. Response surfaces of the log (ACE, MET, and PEN q<sub>e</sub>) on the X<sub>8</sub>-X<sub>9</sub> plane (activation temperature vs. activation time), with X<sub>6</sub> and X<sub>7</sub> (pyrolysis temperature and pyrolysis time, respectively) fixed at level 0.

Table 3		
Response variables,	BET analysis, and porosimetry data for the characterized mater	rials.

Synthesis conditions			Yield	$q_{\rm e \ ACE}$	$q_{\rm e\ MET}$	q <sub>e PEN</sub>	SBET	V <sub>pore</sub>	Average pore width		
Material	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X9	%	$mg g^{-1}$	$mg g^{-1}$	$mg g^{-1}$	$m^2 g^{-1}$	$cm^3 g^{-1}$	Å
	°C	h	°C	min							
Run 1	350	1.5	700	10	29.57	4.4	1.4	103.7	4.66	0.028	243.2
Run 4	350	1.5	850	30	15.65	171.7	91.9	209.5	740.36	0.340	18.4
Run 8	350	4.5	850	30	14.26	157.0	95.3	218.4	622.05	0.300	19.3
Run 12	650	1.5	850	30	14.19	154.6	91.2	187.9	533.04	0.254	19.0
Run 13	650	4.5	700	10	27.39	10.9	5.4	72.1	18.16	0.018	40.1
Run 16	650	4.5	850	30	11.25	160.4	81.4	209.2	608.86	0.280	18.4
Run 22	500	3	850	20	18.44	86.1	27.5	114.0	417.50	0.197	18.9
Run 26	500	3	775	20	24.31	17.5	8.4	74.6	238.72	0.159	26.7
VS	-	-	-	-	-	0.5	0.0	19.7	0.68	0.005	304.6
4 NA	350	1.5	-	-	41.71	4.1	1.0	87.1	1.26	0.006	189.9
4 NCO <sub>2</sub>	350	1.5	850	30	28.09	3.2	0.9	103.5	6.56	0.016	100.6
16 NA	650	4.5	-	-	28.04	5.6	1.6	95.6	4.15	0.014	131.4
16 NCO <sub>2</sub>	650	4.5	850	30	26.69	10.0	7.0	128.9	74.62	0.051	27.4

#### Table 4

Adsorption capacities of different types of adsorbents used for ACE, MET and PEN removal from ultrapure water in single component systems.

Adsorbate	Adsorbent	q <sub>e</sub> (mg g <sup>-1</sup> )	References
ACE	Industrial sewage sludge derived activated carbon	124.3	[43]
ACE	Metal-organic framework (MIL-101(Fe)	57.6	[44]
ACE	Crayfish shell derived biochar	40.41	[45]
ACE	Porous organic polymers (POP)	65.97	[46]
ACE	Commercial activated carbon F400	163.7	[47]
ACE	Vine-pruning derived biochar	171.7	This study
MET	Zeolite	10	[48]
MET	Vine-pruning derived biochar	91.9	This study
PEN	carboxymethyl tragacanth-based hydrogel	196.8	[49]
	Grafed with poly (acrylic acid-co- acrylamide)		
PEN	Commercial clay modified with cationic- surfactant micelles	6.33	[13]
PEN	Vine-pruning derived biochar	209.5	This study

the adsorption of PEN due to the enhancement of the porosity, it is counterproductive due to the reduction of partitioning in partially carbonized biochar fractions. A direct relationship is also evident between size and volume pore and response variables: reduced average pore size and increased  $V_{pore}$ result in lower yields but higher adsorption capacities for pesticides. Run 4, notable for its high pesticide adsorption capacity, features an average pore size of 18.4 Å, placing it within the micropore range. This is consistent with its nitrogen adsorption-desorption isotherm, classified as Type I(a) by IUPAC standards, a reversible isotherm typical of materials predominantly composed of micropores [31], as detailed in Figure S4 from the supplementary material.

In contrast to coals which are composed of crystalline particles forming graphite-like layers, biochar has an amorphous structure [18]. This characteristic allows biochar to have various types of adsorption sites, often exhibiting a heterogeneous distribution. SEM images in Fig. 7 illustrate the morphology of biochar synthesized in runs 1 and 8. Run 8, previously noted in Table 3 for its high  $S_{BET}$  and adsorption capacities for the three pesticides, displays slit-shaped pores or honeycomb structures (see Fig. 7b), typically found in activated biochar [56] and visually confirming the material's extensive microporosity. In contrast, run 1, which has been shown to have almost no  $S_{BET}$  and pesticide adsorption capability, lacks such porous structures.

The ash content in the VS feedstock was determined to be 4.25 %. This value is within the normal range for woody biomass, which



Fig. 7. SEM images of the surface structures of activated biochar. (a-b) Run 8 (c-d) Run 1, with images a and c magnified 1000 times, and b and d magnified 5000 times.

#### Table 5

Elemental analysis for the characterized materials.

Synthesis conditions				Ν	С	Н	0	H/C	O/C	
Material	X <sub>6</sub> °C	X <sub>7</sub> h	X <sub>8</sub> °C	X9 min	%	%	%	%		
Run 1	350	1.5	700	10	1.42	76.92	1.68	9.90	0.022	0.129
Run 4	350	1.5	850	30	2.18	69.47	1.60	13.60	0.023	0.196
Run 8	350	4.5	850	30	2.19	65.53	1.07	14.80	0.016	0.226
Run 12	650	1.5	850	30	2.12	61.94	0.84	18.00	0.014	0.291
Run 13	650	4.5	700	10	1.51	76.23	1.17	11.60	0.015	0.152
Run 16	650	4.5	850	30	2.27	61.95	0.79	13.90	0.013	0.224
Run 22	500	3	850	20	1.97	68.80	1.10	13.50	0.016	0.196
Run 26	500	3	775	20	1.71	76.35	0.89	10.20	0.012	0.134
VS	-	-	-	-	0.92	45.70	5.90	41.60	0.129	0.910
4 NA	350	1.5	-	-	1.26	66.02	4.67	24.20	0.071	0.367
4 NCO <sub>2</sub>	350	1.5	850	30	1.63	81.29	0.89	10.40	0.011	0.128
16 NA	650	4.5	-	-	1.74	64.54	1.76	7.20	0.027	0.112
16 NCO <sub>2</sub>	650	4.5	850	30	1.62	77.08	0.79	11.80	0.010	0.153

typically exhibits low ash contents (less than 7 %) [57]. Higher amount of ash content in biomass feedstock is negatively correlated with the  $S_{BET}$  in the resulting biochar, as ashes partially fill or block micropores [58, 59].

Table 5 presents the elemental analysis of the selected materials, as well as the H/C and O/C ratios.

It is widely documented in the literature that higher pyrolysis temperatures enhance the carbon content in biochar through dehydration and deoxygenation of biomass, simultaneously reducing hydrogen and oxygen functional groups. This process lowers the O/C (indicator of polarity) and H/C (indicator of aromaticity) ratios, resulting in a more hydrophobic and aromatic biochar [51,60]. The carbon content of non-activated material 4 NA increases from 66.02 % to 81.29 % when activated at 850 °C with N2 instead of CO2 (material 4 NCO2). However, this carbon content reduces to 69.47 % in run 4, which is subjected to a CO<sub>2</sub> atmosphere, owing to the selective carbon elimination through the Boudouard reaction. Despite these findings, there is no significant correlation between elemental composition or O/C, H/C ratios, and the adsorption capacity in FCCD runs. This may be due to the activation stage, which, regardless of the varying pyrolysis conditions, consistently exposes all materials to temperatures between 700 and 850 °C in CO<sub>2</sub> atmospheres, thus homogenizing the hydrogen and oxygen content.

The FTIR spectra of VS and activated biochar from runs 1, 4, 6, 8, 12, 16 and 13 are presented in Fig. 8.

The infrared (IR) spectra of activated biochar reveal a notable reduction in chemical diversity compared to the raw material, resulting in a product that is predominantly aromatic with diminished hydrogen content. For example, all biochar samples exhibit a decrease in the stretching vibrations of O–H ( $3200-3500 \text{ cm}^{-1}$ ) and C–H (at 2900 cm<sup>-1</sup>). This trend is attributed to dehydration reactions occurring within the biomass, implying a reduction in polar functional groups [51].

Materials with higher adsorption capacities (runs 4, 8, 12 and 16) exhibit greater intensity in some spectral peaks compared to materials with lower porosity and adsorption capacity (runs 1 and 13). A pronounced peak at 1422 cm<sup>-1</sup>, related to the (C=C) stretching in aromatic rings [42,61,62], confirms the presence of aromatic structures. Adjacent, broad bands ranging from 990 to 1060 cm<sup>-1</sup> are attributed to (=C-O-C) stretching present ether-like structures. Furthermore, a distinct sharp band near 866 cm<sup>-1</sup>, possibly linked to (C-H) ring bending, is accompanied by signs of aromatic C-H stretches in the characteristic range of 3000–3100 cm<sup>-1</sup> [61].  $\pi$ – $\pi$  interactions, which are intermolecular attractions between electron-rich  $\pi$ -systems, are proposed as one of the primary mechanisms underlying the adsorption of the pesticides onto activated biochar [63]. Low H/C ratios and the presence of aromatic groups, as found by IR spectroscopy, suggest an interaction between the  $\pi$  electrons in the aromatic structure of the adsorbent and the aromatic ring of the adsorbate. Specifically, in the case of ACE, the  $\pi$ - $\pi$  interactions occur with its pyridine ring, whereas in MET and PEN, these interactions occur with their respective benzene rings [64,65]. On the other hand, hydrogen bonding may be also formed between an electronegative atom (like C-O functional group present on the biochar surface) and a hydrogen atom bonded to a second electronegative atom in the pesticide's molecules.



Fig. 8. Spectra Peaks in Fourier-Transform Infrared (FTIR) Analysis: Comparison of VS with Runs 1, 4, 8, 12, 13, and 16 from the FCCD.

# 3.3. Balancing synthesis yield and adsorption performance: optimization and practical considerations

The inverse relationship between biochar synthesis yield and adsorption capacity, as shown in Fig. 2 and Figures S2 and S3 from the supplementary material, is critical in large-scale applications. Higher activation temperatures and longer activation times enhance adsorption by increasing surface area and porosity but reduce biochar yield due to carbon loss. Thus, optimal synthesis conditions must be carefully selected based on the intended application, as processing costs significantly impact economic feasibility [66]. Multi-objective optimization approach, such as Pareto front optimization, can help balance yield and adsorption performance by identifying optimal trade-offs [67]. However, the optimization boundaries must be defined according to the final application.

To further explore this balance, biochar adsorption capacity per gram of precursor biomass processed ( $q_{e,biomass}$ ) was analysed. Using  $q_{e,biomass}$  as a response variable in the FCCD, coefficient weights were obtained (Figure S5 from the supplementary material), showing that for ACE and MET, they are similar to adsorption capacity per gram of biochar ( $q_e$ ). This means that only high  $q_{e,biomass}$  and  $q_e$  values are achieved under high activation conditions, reaching, for example, 26.9 mg g<sup>-1</sup> biomass for ACE and 14.4 mg g<sup>-1</sup> biomass for MET in Run 4 (850 °C, 30 min), highlighting its dependence on porosity development.

For PEN, however, the coefficient weights differ significantly, with a reduced activation effect and an increased negative influence of pyrolysis temperature on  $q_{e,biomass}$ . For example, in run 4, PEN  $q_{e,biomass}$  is 32.8 mg g<sup>-1</sup> biomass, while in run 1, it remains high at 30.7 mg g<sup>-1</sup> biomass. However, run 1, synthesized under low activation conditions (700 °C, 10 min), resulted in a significantly higher yield (29.57 %) while consuming considerably less energy and gas than Run 4 (yield:15.65 %; activation conditions: 850 °C, 30 min). These findings suggest that for hydrophobic compounds like PEN, optimizing synthesis conditions to maximize biochar yield can be more sustainable and cost-effective, even if adsorption capacity is reduced. This highlights the importance of adjusting biochar production parameters based on the specific contaminants targeted in adsorption applications.

From a scalability perspective, transitioning from lab-scale batch pyrolysis to industrial-scale production requires process intensification strategies, such as optimizing gas flow rates, recovering heat from pyrolysis gases, and integrating biochar activation with by-product utilization, like bio-oil, to enhance overall efficiency. Bio-oil, a by-product of biomass pyrolysis, contains valuable compounds and can be partially used for heat recovery, reducing reliance on external energy sources [68]. Cost reduction in biochar activation could be achieved by utilizing  $CO_2$  from wine fermentation. During winemaking, fermentation releases approximately 84.5 g of  $CO_2$  per litter of must [69]. This  $CO_2$  could serve as a renewable and cost-effective activation gas, reducing reliance on fossil-derived  $CO_2$ . While  $CO_2$  recovery in winemaking have been studied [70–72], their specific application in biochar activation has never been explored, highlighting the need for dedicated studies on this topic.

Considering adsorption efficiency, biochar yield, and scalability potential, vine-pruning-derived biochar emerges as a promising, lowcost adsorbent for pesticide remediation. Future research should focus on pilot-scale validation, life-cycle assessment, and techno-economic feasibility to ensure its viability for large-scale applications.

# 4. Conclusions

This study evaluated nine operational parameters in synthesizing activated biochar from vine shoots. Experimental design determined the significance of these variables in pesticides ACE, MET, and PEN adsorption and biochar yield. A Plackett-Burman screening showed that pyrolysis flow rate and feedstock particle size have no significant impact. However, a reducing pyrolysis atmosphere and high CO<sub>2</sub> flow

during activation enhance MET adsorption in biochar. This effect is minor compared to the height of biomass in the oven: greater heights result in higher yields but lower pesticide adsorption due to limited  $CO_2$  diffusion.

Using a FCCD, obtained models showed that activation factors (temperature and time) are crucial for both yield and adsorption capacity, while pyrolysis duration (1.5–4.5 hours) does not significantly impact adsorption. At activation temperature of 850 °C, carbon is rapidly removed from biochar's surface, improving S<sub>BET</sub>, V<sub>pore</sub>, and microporosity.

The FCCD optimized the biochar production, achieving equilibrium adsorption capacities of 171.7, 91.9, and 209.5 mg  $g^{-1}$  for ACE, MET, and PEN, respectively, with a 15.65 % synthesis yield. Optimal synthesis conditions to achieve the highest adsorption capacities were low pyrolysis (350 °C for 1.5 hours) and high activation (850 °C for 30 minutes). However, for applications that do not require high adsorption capacities for hydrophobic compounds like PEN, lower activation conditions could be used to reduce energy and gas consumption, since high adsorption capacities per gram of biomass processed are also achieved. The biochar characterization revealed its hydrophobic and aromatic nature, suggesting  $\pi$ - $\pi$  interactions and hydrogen bonding for ACE and MET adsorption, with hydrophobic interactions and partitioning being significant for PEN. The favourable results obtained for all compounds indicate that these optimal synthesis conditions may apply to other biomass sources with similar lignin and ash content, pending further validation. Moreover, the activated biochar could potentially exhibit strong performance with other pesticides, regardless of their hydrophilic nature, as seen with ACE and MET, and specially with hydrophobic compounds, as observed with PEN. These findings confirm that DoE is a suitable tool for optimizing and modelling biochar synthesis. Additionally, VS emerged as a potential biochar feedstock, surpassing other adsorbents and performing similarly to commercial activated carbon.

#### CRediT authorship contribution statement

Sans Carme: Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition. Bayarri Bernardí: Writing – review & editing, Validation, Supervision, Resources, Project administration, Data curation, Conceptualization. Leardi Riccardo: Writing – review & editing, Validation, Software, Methodology, Formal analysis. Llopart-Roca Pere: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Autó Emma: Visualization, Methodology, Investigation, Formal analysis.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the

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### Data availability

Data will be made available on request.

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