Influence and modeling of operational parameters on the synthesis yield and adsorption capacity of biochar derived from vine prunings

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1. Background and purpose of the work

Viticulture is a significant economic activity in Europe, where it stands as a global leader. As a consequence of this activity, in Spain alone, approximately 2 million tons of vine shoots are generated each year. Despite efforts to promote the valorization of this residue, the majority still ends up being burned. The valorization of vine shoots into biochar offers a sustainable solution for this agricultural waste, leveraging its capacity for carbon sequestration and its application in improving soil quality, energy production, and pollutants removal. Specifically, biochar emerges as a cost-effective, efficient adsorbent of compounds of emerging concern (CEC) such as pharmaceuticals and pesticides found in water, which endanger human health and environment.

This study focuses on using vine shoots as a biomass feedstock for the production of biochar, activated with CO_2 in order to increase its adsorption capacity. Unlike traditional one-variable-at-a-time methods, an emphasis is placed on employing a Design of Experiments methodology for the efficient identification of key factors and their interactions, aiming to achieve optimal synthesis conditions with a minimal number of experiments. The work is divided in two stages. Initially, the Plackett-Burman design (PBD) is employed to analyse the importance of variables usually overlooked, studying biomass quantity, particle size, pyrolysis gas flow and composition, and activation gas flow, specifically applied to the adsorption of common fungicides. In a second part, a Face-Centered Central Composite Design (FCCD) is employed to comprehensively examine the weight and interaction of the four main variables: temperature and time of pyrolysis and activation. Synthesis yield and adsorption capacity are chosen as response variables. Through a comprehensive analysis involving Design of Experiments methodology, the study identifies significant, novel factors affecting activated biochar's synthesis yield and adsorption capacity, providing valuable insights for future applications in environmental remediation and sustainable agriculture practices.

2. Material and methods

Vine shoots underwent a process of washing, sieving, and drying. For the PBD screening, a weighted fraction of the biomass was subjected to pyrolysis using N_2 at 500 ºC for 4 hours, and then activated with CO_2 at 800 ºC for 1 hour. For the FCCD, this process was repeated by adjusting the pyrolysis and activation time and temperature as shown in table 1. In FCCD experiments, 10 g of biomass were utilized, with only N_2 and CO_2 employed and maintaining a fixed flow of 4 L/min.

Acetamiprid (ACE), Metalaxyl (MET), and Penconazole (PEN) adsorption capacity on activated biochar were selected as response variables, since they are pesticides of varying hydrophobicity (log Kow = 0.8, 1.65 and 3.72 for ACE, MET and PEN respectively) found in treated wastewater, with interest from an environmental and human health point of view. Analytical standards from Sigma-Aldrich were used. The synthesis yield, calculated by dividing the amount of biochar obtained by the amount of initial biomass, was the second variable response. Chemicals used were of analytical grade from Panreac Química (Spain). Nitrogen, reductant gas (N_2/H_2 95:5 mixture), and carbon dioxide gases were supplied by Abelló Linde (Spain). Milli-Q water was obtained using a filtration system from Millipore (USA). The CAT software (Chemometric Agile Tool, version of September 5, 2023) was employed for processing the data obtained from the experimental designs.

Adsorption capacities were estimated through batch adsorption experiments in 250 mL solutions with an initial pesticide concentration of 0.08 mmol/L. The pH was fixed at 7 using a buffer, and the biochar dosage was 50 mg/L. The solutions were shaken for 72 hours at 25 ºC until equilibrium, measuring the concentration through High-Performance Liquid Chromatography (HPLC). Biochars were characterized using elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, and porosimetry.

3. Results and discussion

The PBD indicated that among factors such as initial biomass quantity (7 or 14 g), biomass particle size (125 or 250 µm), pyrolysis gas composition (99.99% N2 or 95:5 N2:H2), and pyrolysis and activation gas flows (2 or 6 L/min), only the initial biomass quantity ($p < 0.001$) significantly influenced both synthesis yield and pesticide adsorption capacities. Increasing the biomass in the furnace enhanced synthesis yields but reduced pesticides adsorption capacities. This effect is due to the larger biomass quantity impeding the diffusion of the activating agent (CO_2), limiting porosity development through the Boudouard reaction.

In the FCCD, a model elucidating the synthesis yield's dependence on pyrolysis and activation temperature and time was developed, obtaining an adjusted R^2 of 0.99 and a residual standard deviation of 0.47. This model highlighted that the activation temperature and time ($p < 0.001$) are crucial for yield. Also, a pronounced negative interaction was found: at low activation temperatures (700 ºC), activation time has minimal impact on yield (29.57% in run 1), whereas at high activation temperatures (850 ºC), the activation time is crucial (15.65% in run 4). Table 1 presents the yield values obtained for the different materials synthesized.

Related to the adsorption capacity of ACE, MET, and PEN, accurate models with adjusted R^2 values of 0.98, 0.96, and 0.89, and residual standard deviations of 0.07, 0.11, and 0.05, respectively, were obtained. Activation conditions predominantly determined the biochar's final adsorption capacity, with the pyrolysis step having a small effect. As shown in Table 1, only experiments conducted at high activation temperatures and times (850 ºC and 30 minutes) achieved high adsorption capacities for all compounds, attributed to the development of an extensive, predominantly microporous, surface area. With 740.36 $m^2 g^{-1}$ the biochar from Run 4 demonstrated significant adsorption capacities per gram of biochar: 171.7 mg for ACE, 91.9 mg for MET, and 209.5 mg for PEN.

Table 1. Response variables, BET analysis, and porosimetry data for the characterized materials. "F" and "G" are the pyrolysis temperature and time, while "H and "I" are the activation temperature and time.

Material	Synthesis conditions				Yield	$q_{e\,ACE}$	$q_{e\,MET}$	$q_{e\,PEN}$	S_{BET}	V_{pore}	Average pore width
	F	G	H	I							
	◦C	h	◦C	min	%	mg g^{-1}	mg g^{-1}	mg g^{-1}	$m^2 g^{-1}$	$cm^3 g^{-1}$	Å
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

The characterization of the biochar revealed its hydrophobic and aromatic characteristics, suggesting π–π interactions and hydrogen bonding as the primary mechanisms for the adsorption of ACE and MET, while hydrophobic interactions and partitioning play a significant role for PEN. SEM images showcased the biochar's typical slit-shaped pores or honeycomb-like structures, and an extensive porosity.

These results emphasize the potential of vineyard shoots as a valuable resource for producing activated biochar. This research has comprehensively investigated and modelled the key factors involved in synthesizing activated biochar with CO_2. Through a meticulous experimental approach, the study has elucidated the impact of these variables on both the adsorption efficiency for various organic micropollutants and the overall yield of the biochar, demonstrating the practical applicability and efficiency of VS in biochar synthesis.

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