

Hydrothermal Carbonization Conditions Parameters Optimization Using RSM–CCD for preparation of biofertilizer materials from olive solid wastes

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Abstract. Olive solid wastes (OSW), a low-cost biomass, were utilized to prepare a biofertilizer by hydrothermal carbonization. In the present study the effect of temperature (ranging from 170 to 240 °C) and residence time (ranging from 17 to 103 min) on hydrochar production was studied to maximize the solid yield. The study employed a central composite design (CCD) response surface method (RSM) to optimize temperature and residence time of hydrothermal carbonization process for enhancing hydrochar yield and quality, to be used as a biofertilizer in the culture media. Response surface methodology (RSM) was applied to investigate the effect of operational parameters (temperature and residence time) on the solid yield. The results showed that a maximum hydrochar yield output of 57.4 % was obtained at 171 °C and during 35 minutes. High HTC temperature (240°C) promotes a low pH as well as the content of ash, but generates high electrical conductivity (EC). The predicted reduced cubic model for response variables was found to be significant ($p < 0.01$), and the analysis of variance (ANOVA) showed a high coefficient of determination with R^2 being 0.99 for biomass. The three phases obtained were then characterised by various analytical techniques and the hydrochar was evaluated as a biofertiliser, via phytotoxicity tests on lettuce seeds (*Lactuca sativa*). Phytotoxicity tests revealed significant toxicity of the aqueous extracts, whereas washing significantly reduced the phytotoxicity of the hydrochars by eliminating the water-soluble toxic compounds.

1 Introduction

In the climate change context and the circular economy, agricultural and environmental uses of hydrochar have generated considerable interest. Hydrochar has unique characteristics such as its pH, water-holding capacity, surface charge, and nutrients. This study reviews the production of hydrochar from olive solid wastes (OSW) by Hydrothermal carbonization (HTC), its environmental application, chemical and physical characterization. This work

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studies the production conditions of hydrochar from olive solid wastes, by studying the HTC reaction time and temperature effects on the hydrochar’s physico-chemical properties.

The most widely used statistical method is the response surface method (RSM), because it studies the interactions between one or more inputs and outputs variables, and it also interprets response results on non-linear surfaces. This method generally includes design of the experiment, development of response model, and analysis of variance. Furthermore, RSM analysis includes different models, and in this article, we adopted the centered composite design (CCD) because, with a small number of experiments in a specified range, it allows us to predict responses and capture variables. To determine the interaction of many variable influences, the Response Surface Methodology (RSM) uses statistical methods, which offers a precise and efficient research approach.

The assessment of the toxicity of various environmental compounds and substances through the analysis of plant seeds. Water and air are carried out using a crucial method called phytotoxicity.

This method is used to assess the toxicity of water, industrial waste, and biosolids, using plant species as control organisms through the analysis of their root growth. In our study, the presence of phytotoxic substances in hydrochars was assessed using several germination tests, following the procedure described by Zucconi et al. [1]

2 Materials and methods

2.1 Raw material preparation

Olive solid waste (OSW) resulting from the olive oil extraction process are collected after the pressing phase, in November. In our study, OSW are collected in southern Tunisia (Gabès). These residues are carefully submerged with hot water to eliminate any oil residue or any impurities.

After cleaning, the OSW are air-dried to reduce and homogenize its moisture content while maintaining its nutritional properties. All raw biomass were sieved to ensure a uniform particle size. Finally, the homogenized samples were stored under ambient conditions, in clean plastic jars, to further experiments

Table 1. Olive solid waste’s elemental analysis

Element Content(%Wt)					
C	H	O	N	S	Ref
43.1	7.1	47.4.	0.4	0.8	[2]
48.3	6.73	43.71	1.26	-	[3]
46.6	5.9	46.1	1.4	-	[4]

2.2 Hydrochar preparation

Hydrothermal carbonization experiments (Figure 1) were performed under autogenic pressure in a 300 ml Lab-scale stainless steel autoclave equipped with thermometer and pressure gauge. The sample was mixed with distillate water; a biomass/water mass ratio of 1/8 is established by mixing 25 g of OSW with 200 g of distilled water, then was loaded into the reactor, the screws are securely tightened, after that the reactor is placed on the preheating furnace.

The heat treatment applies temperatures and reaction time ranging from 170 °C to 240 °C and 30 to 103 minutes, with CCD factor levels described in **Section II.3**. As soon as the predetermined temperature of the reactor reached, it was held steady at that level throughout

the duration of the residence time. At the end of the reaction time, the heating system has stopped working, and the stainless-steel autoclave was placed in ice bath to stop the reaction, where it remains until it reaches room temperature (about 15 minutes).

Once cooled, the solid formed and the liquid are separated by filtration, and then rinsed with water until a clear filtrate is obtained. Thereafter, it is dried in an oven overnight at 105 °C to remove any remaining moisture. Dried HC is stored in a sealed plastic bag.

The solid yield (SY, % wt) is determined as the ratio between the weight of the initial biomass (m_0) and HC's final weight (m_f), after filtration of the liquid phase and drying.

HCs are coded with HC-T-t, where, T represents the temperature, and t represents the reaction time, HC-170-30, for example, is produced at 170 °C for 30 minutes

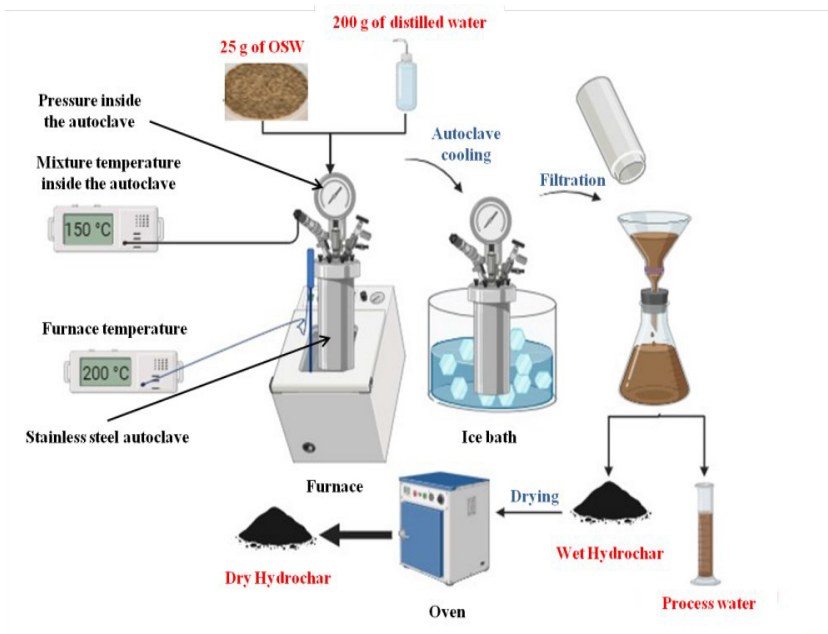


Fig. 1. Hydrothermal carbonization process

2.3 Experimental Design of (DOE): Modeling of OSW Experiments HTC Process Optimization

Optimizing HTC operating conditions is essential to ensure efficient use of raw materials and obtain high-quality finished products. Based on the response surface methodology (RSM) the OSW's HTC experimental design was placed using a central composite design (CCD) to evaluate the curvature effect on the correlation between solid phase yields and operating parameters. Composite central design (CCD) is implemented using a two-level fractional factorial (± 1) from the center point (0), supplemented by a group of axial points spaced $|\alpha| \geq 1.414$.

Based on researchers and preliminary experiments using the same sample, the operating conditions, parameters choice, and their ranges are regrouped on Table 2. To achieve optimal HTC conditions, this study examined two of the most important parameters, reaction temperature and residence time. To this end, we proposed CCD, and we include the following ranges of each parameter: (a) temperature: 170–240°C; (b) reaction time: 17–103 min. The Design-Expert 13 software selects these various experimental assemblies as an experimental matrix.

Table 2. The CCD HTC experiments Factors levels.

Factors	Symbols	Units	Coded and Un-Coded Factor Level				
			-1.414 (- α)	-1	0	+1	+1.414 (+ α)
Temperature	T	°C	170	180	205	230	240
Residence time	t	min	17	30	60	90	103

Using a second-order polynomial equation, data regression analysis was based on. In the variance analysis (ANOVA), the probability and fisher’s test values (p-value and F-value respectively) are the basis to examine the main interaction effects and variables in the equation. Additionally, regression analysis parameters were examined, including the predicted R^2 , adjusted R^2 , and determination coefficient (R^2).

2.4 Analytical methods

To determine the pH and electrical conductivity (EC) of both raw material and HCs. aqueous extracts were prepared (using 1 to 10. wt/v ratio) by dispersing 1 g of powdered HC in 10 ml of distilled water. The resulting suspensions were stirred mechanically for 2 hours. Then was centrifuged for 10 minutes at 6000 rpm to promote phase separation. allowing for the extraction of the supernatant.

After that, the pH and EC of the filtrates were then measured using a digital pH meter (AZ Instruments), and conductivity meter (EUTECH Instruments), respectively.

2.5 Data analysis

Three responses of solid yield (%), pH of hydrochars produced and germination index (GI%) were evaluated as biofertilizer properties of hydrochars. The SY shows the recovered solids quantity after HTC. The response was calculated as the ratio between initial biomass mass (m_0) and final HC mass (m_f), after filtration of the liquid phase and drying.

The toxicity assessment of various environmental compounds and substances through the analysis of plant seeds, water, and air is carried out using a crucial method called phytotoxicity. This method is used to evaluate the toxicity of industrial waste, biosolids, and water by analyzing plant root growth.

The growth index or germination index (GI%), which has an inverse relationship with the degree of examined samples toxicity, is essential for this assessment. The lower the GI, the more toxic the compound, as it completely or partially inhibits seed root growth [5].

3 Results

3.1 Statistical validation model

According to CCD experimental design, the HTC process was optimized included three replicates of the central points and 8 factorial points. Table 3 depicted the operating conditions of the set of tests launched, the range for each variable. The modelling results showed a good agreement between predicted values from CCD model and experimental results. Indicating experimental results adequacy with the proposed model.

Variance analysis ANOVA was applied to examine the sufficiency and statistical assessment of the significant variables for the model that was anticipated. Table 4 represents the characteristics of the statistically significant terms of the selected model. From the analysis data, due to the p-value lower than 0.05, T, t, and Tt^2 are significant terms.

The model of SY prediction (Table 4) is significant and fit the experimental data well, as confirmed by the high values of the coefficient of determination (R^2), which are very close to 1 ($R^2 = 0.9984$). The Predicted R^2 of 0.9150 and the Adjusted R^2 of 0.9945 are in agreement, because that the difference is less than 0.2. Moreover, adequate precision measures the signal to noise ratio. A ratio higher than 4 (53.964 in this case) indicates an adequate signal.

In the present reduced cubic model, the temperature and residence time are significant parameters with p-values <0.0001 and 0.0034 respectively.

Moreover, the model of pH (Table 5) prediction is significant and fit the experimental data well, as confirmed by the great coefficient of determination values (R^2), which are very close too to 1 ($R^2 = 0.9801$). The Predicted R^2 of 0.8592 and the Adjusted R^2 of 0.9602 are in agreement, the difference is less than 0.2. Moreover, adequate precision measures the signal to noise ratio. A ratio greater than 4 (20.8343 in this case) indicates an adequate signal.

In present quadratic model, the temperature and residence time are significant parameters with p-values <0.0001 and 0.004 respectively.

Table 3. Coded design matrix including the corresponding responses.

Std. Order	Run Order	FactorS		Factor		Response (R)		
		A	B	T (°C)	t (min)	SY (%)	pH	IG
11	2	0	0	205	60	49.1	4.81	21.01
2	3	+1	-1	230	30	46.6	4.58	2.72
5	1	-1.414	0	170	60	57.1	6.52	19.5
9	4	0	0	205	60	49.36	4.84	22.1
6	8	+1.414	0	240	60	40.56	3.9	1.13
10	11	0	0	205	60	49.48	4.8	21.25
7	10	0	-1.414	205	17	51.52	5.25	11.8
4	5	+1	+1	230	90	42.2	4.1	13.87
1	7	-1	-1	180	30	54.76	6.36	10.73
3	9	-1	+1	180	90	51.24	5.82	18.41
8	6	0	+1.414	250	103	47.2	4.2	29.82

Table 4. ANOVA for prediction of SY by the reduced cubic model

Settings	Statistics					
	Squares Sum	Freedom Degree	Mean Square	F-value	p-value	
Model	236.61	7	33.80	261.68	0.0004	significant
T	136.79	1	136.79	1058.94	< 0.0001	
t	9.33	1	9.33	72.24	0.0034	
Tt	0.1936	1	0.1936	1.50	0.3082	
T ²	0.6544	1	0.6544	5.07	0.1099	
t ²	0.0321	1	0.0321	0.2486	0.6523	
T ² t	0.4098	1	0.4098	3.17	0.1729	
Tt ²	4.79	1	4.79	37.09	0.0089	
Residuals	0.3875	3	0.1292			
Lack of Fit	0.3120	1	0.3120	8.27	0.1026	not significant
Pure Error	0.0755	2	0.0377			
Cor Total	237.00	10				
Std. Dev.		0.3594	R²			0.9984
Mean		49.01	Adjusted R²			0.9945
C.V. %		0.7333	Predicted R²			0.9150
			Adeq Precision			53.9638

Table 5. ANOVA for prediction of pH by the Quadratic model

Settings	Statistics					
	Squares Sum	Degree of freedom	Squares Sum	F-value	Squares Sum	
Model	7.67	5	1.53	49.30	0.0003	significant
T	6.49	1	6.49	208.44	< 0.0001	
t	0.7843	1	0.7843	25.19	0.0040	
Tt	0.0009	1	0.0009	0.0289	0.8717	
T ²	0.3775	1	0.3775	12.12	0.0176	
t ²	0.0015	1	0.0015	0.0467	0.8375	
Residuals	0.1557	5	0.0311			
Lack of Fit	0.1548	3	0.0516	119.07	0.0083	significant
Pure Error	0.0009	2	0.0004			
Cor Total	7.83	10				
Std. Dev.		0.1764	R²			0.9801
Mean		5.02	Adjusted R²			0.9602
C.V. %		3.52	Predicted R²			0.8592
			Adeq Precision			20.8343

Figure 2 shows the diagram parity of the experimental design. The plot of actual versus the predicted data of solid yield (SY). The plots proves that experimental data points lie very well to diagonal line this can indicates good agreement between the theoretical and experimental values

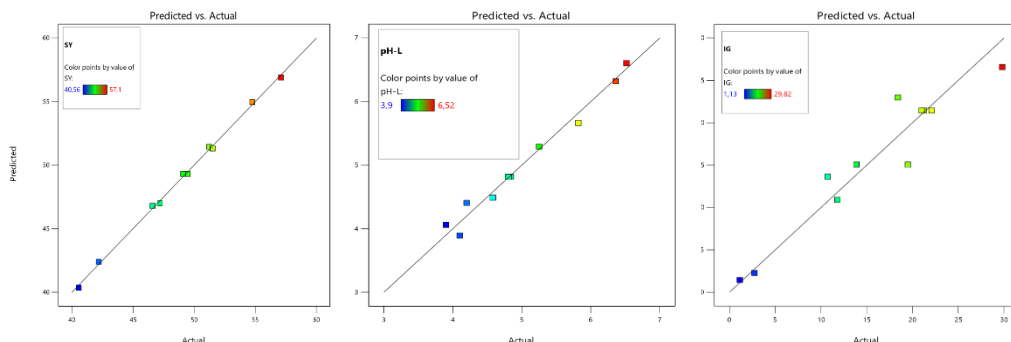


Fig.2. Predicted versus actual value response for solid yield (SY), pH, and Germination Index

Based on this statistical analysis, we can affirm that the experimental results agree with the obtained models, which are presented in Table 4 and Table 5.

Using Design Expert software, the relationship between the response and the variables was established and expressed by a reduced cubic model. The cubic models used to predict the solid yield (SY) as a function of the coded variables are regrouped in Table 6.

Table 6. SY models in actual and coded factors.

Response Variable	Obtained Models
SY	SY(%) $=236.61+136.79T+9.33t+0.1936Tt+0.6544T^2+0.0321t^2+0.4098T^2t+4.79Tt^2$
pH	$pH =7.67+6.49T+0.7843t+0.0009Tt+0.3775T^2+0.0015t^2$

Fig. 3 shows a comparison between observed and predicted values. The strong correlation between these two values demonstrates the model's effectiveness.

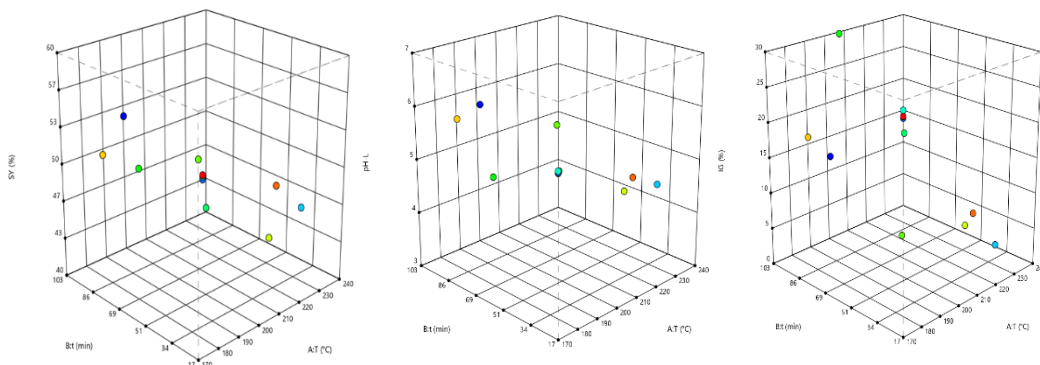


Fig.3. Different variables interaction effects on SY (a), pH (b), and the germination Index (c) using 3D response surface.

To evaluate the difference between the observed and predicted response values, the main figures (Fig. 3) were used. Furthermore, Figure 3 helps to verify that the statistical assumptions fit the analysis data. It can be concluded that, for solids yield, the predictions of the experimental data using the developed cubic model are perfectly satisfactory.

3.2 Analysis of Interactive Factors on HTC Process

Figure 4 illustrates the effect of each factor on the response, which is represented by the main effect of the variables.

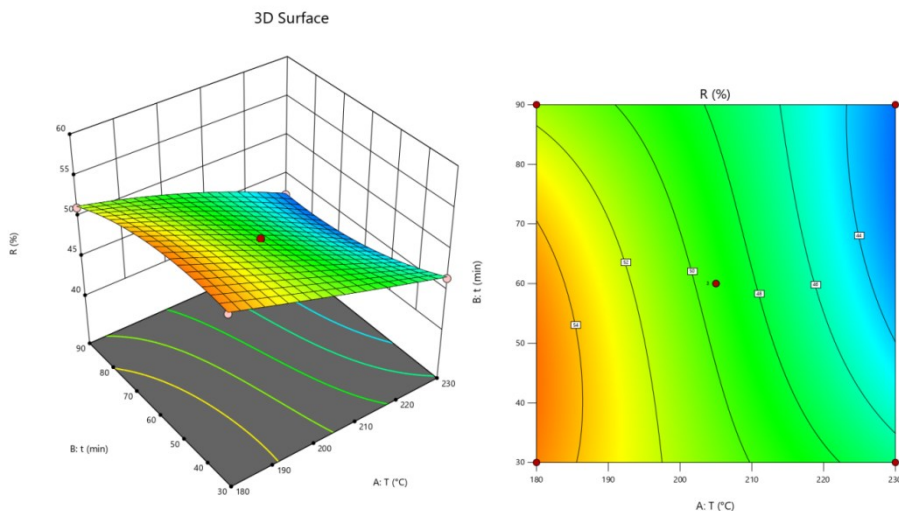


Fig. 4. Different variables interaction effects on SY using 3D response surface and 2D contour plots.

Visual inspection of Figure 4 reveals that the R-squared surface curves of the HCs exhibit an upward-sloping peak surface, This explains why the global maxima or minima are found outside the domain of interest ($-1.414 \leq x \leq 1.414$) [6]. These values are highlighted by the critical coordinates of the first derivative, located at (171°C, 35min), respectively.

Therefore, SY was maximized within the operability and interest domain to maximize SY (%) = 57.4.

4 Conclusion

This study focuses on the sustainable valorization of agro-industrial waste, specifically solid olive waste, using the HCT method.

The main objective is to optimize the process operating conditions to improve the quantity and quality of the HCs produced, while also examining its potential uses as a biofertilizer.

Through optimization using the response surface method (RSM), the optimal operating conditions were determined: an approximate temperature of 171 °C and a reaction time of 35 minutes, allowing for a maximum solid yield of 57.4%. Furthermore, analysis of the hydrothermal fluid demonstrated an acidic pH (3.33–3.68) that increases with temperature, associated with the organic acids production and the dissolution of minerals.

However, phytotoxicity tests revealed significant toxicity, primarily due to the presence of water-soluble organic compounds (acids, phenols, aldehydes) generated during HCT. This explains the importance of post-HCT treatments (washing, aging) before any application as a biofertilizer.

References

1. F. Zucconi, A. Monaco, M. Forte (1985) Phytotoxins during the stabilization of organic matter. *Environmental Science, Chemistry*
2. Ghouma I, Jeguirim M, Dorge S et al (2015) Activated carbon prepared by physical activation of olive stones for the removal of NO₂ at ambient temperature. *Comptes Rendus Chim* **18**:63–74. <https://doi.org/10.1016/j.crci.2014.05.006>
3. A.S. Erses Yay, B. Birinci, S. Açıklın, K. Yay, Hydrothermal carbonization of olive pomace and determining the environmental impacts of post-process products, *J. Clean. Prod.* **315** (2021), <https://doi.org/10.1016/j.jclepro.2021.128087>.
4. S. Bas, akçılardan Kabakçı, S.S. Baran, Hydrothermal carbonization of various lignocellulosics: Fuel characteristics of hydrochars and surface characteristics of activated hydrochars, *Waste Manag.* **100** (2019), <https://doi.org/10.1016/j.wasman.2019.09.021>.
5. P.M. Mendes, J.A. Ribeiro, G.A. Martins, T. Lucia, T.R. Araujo, M.D. Fuentes-Guevara, L.B. Corrêa, et É.K. Corrêa. (2021). Phytotoxicity Test in Check: Proposition of Methodology for Comparison of Different Method Adaptations Usually Used Worldwide. *Journal of Environmental Management* **291**:112698. <https://doi.org/10.1016/j.jenvman.2021.112698>.
6. M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, et L.A. Escaleira. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* **76** (5): 965-77. <https://doi.org/10.1016/j.talanta.2008.05.019>.