

Multi-objective optimization of pyrolysis process of Prosopis farcta under non-isothermal conditions

Ataallah Khademalrasoul^{1*}, Seyed Mohammad Safieddin Ardebili²

¹Soil Science Department, Faculty of Agriculture, Shahid Chamran University of Ahvaz, Ahvaz, Iran ² Biosystems Engineering Department, Faculty of Agriculture, Shahid Chamran University of Ahvaz, Ahvaz, Iran

ARTICLE INFO

Article history: Received 7 February 2021 Received in revised form 18 July 2021 Accepted 20 July 2021

Keywords: Biochar Prosopis farcta Waste management Heating rate Response surface method

ABSTRACT

Biochar is a recalcitrant substance that is produced through the pyrolysis process. The location of this study was Ahvaz in the central part of Khuzestan Province, Iran. To produce biochar, the biomass of Prosopis farcta was pyrolyzed at a temperature of 400°C to 800°C using the heating rate of 3 to 7 °C/min. Afterward, the electrical conductivity, cation exchange capacity, pH, specific surface area, and organic carbon of the biochar were recorded by employing standard methods. The pyrolysis factors such as temperature and heating rate were optimized using the Response Surface technique. Based on the results obtained, the temperature of the process was the most effective variable on the biochar characteristics. Besides, the temperature had a more substantial effect on the structure of the biochar than the heating rate. Also, the modeling results indicated that by enhancing the pyrolysis temperature, the electrical conductivity (EC)/pH of the produced biochar was enhanced mainly due to the concentration effect and reduction of acidic functional groups. With the strengthening of the pyrolysis temperature and heating rate, the organic carbon and specific surface area of the biochar were enhanced, while the cation exchange capacity decreased. According to the obtained results, the best model was found to be a quadratic model. In addition, the model for the EC parameter with the P-value of 0.0004 had the lowest effect compared with other studied pyrolysis factors. In general, the conditions of the pyrolysis process had a remarkable impact on the biochar characteristics; therefore, the effectiveness of biochar can be regarded as an organic amendment. To the best of the authors' knowledge, the present work is the first report assessing the effect of heating rate/ temperature on the biochar characteristics produced from Prosopis farcta.

1. Introduction

Waste management plays an essential role in sustainable development worldwide; therefore, there is a need to focus on the applied aspects of sustainability on different scales. Regarding the importance of soil as the main natural resource to conserve water and provide nutrients for plants, it is vital to apply convenient management scenarios. Organic management, which is based on the application of different decomposed organic materials to ameliorate soil conditions, is the typical form of sustainable management. Biochar is generated as a by-product of the pyrolysis process [12,13]. The pyrolysis process procreates a broad spectrum of solid (char), liquid, and gas components with numerous applications in the direction of sustainable management purposes [27,28,10]. Indeed, the temperature of pyrolysis and the heating rate meaningfully influence biochar characteristics. Generally, pyrolysis consists of three main generation processes: fast, intermediate, and slow [13]. The main solid production of pyrolysis consist of ash, char, and unchanged biomass material, which are named biochar. Biochar can be made from various feedstocks under different processing conditions such as pyrolysis temperature, heating rate, and biomass characteristics (e.g., particle size and hardness) [1,2,4]. As biochar has a porous structure that results in a high specific surface area [3] and a high cation exchange capacity as a consequence of having functional groups [14,15,19], it could effectively increase the capacity of treated soil [20,23]. Nowadays, the emission of greenhouse gases (GHGs) is a global subject for environmental sciences; on the other hand, biochar is a source and sink of carbon simultaneously. Therefore, the production and application of biochar is a convenient non-structural management practice to mitigate GHGs emissions [14, 15]. Biochar can ameliorate soil properties; therefore, it is capable of protecting soil against erosive forces [11]. Despite general properties for biochar, according to pyrolysis conditions, the biochar properties could be disparate [8,16]. The gas produced during pyrolysis in higher temperatures and longer residence times is more than that in lower temperatures and slower heating rates. Bridgwater et al. stated that the pyrolysis conditions are

effective on its yields for different feedstock [4]. Similarly, Demirbas revealed that the amount of char produced from the pyrolysis process diminished when the temperature was enhanced; therefore, they concluded that temperature influenced biochar characteristics [6]. Other research confirms that the pyrolysis conditions are the most influential variables on the biochar characteristics [18, 20]. Therefore, by varying conditions like chemical and temperature in the pyrolysis process, the structural characteristics of biochar change. Prosopis farcta is a species of the genus Prosopis that mostly grows in the Middle East. Regarding the climate conditions of Ahvaz, Prosopis farcta is a resistant plant cover with high potential to produce waste biomass. Biomass conversion into biochar can be influenced by different parameters, including temperature, heating rate, and pressure. A multi-variate statistic method such as Design of Experiments (DoE) could provide thorough/precise knowledge on the biomass pyrolysis process compared to the linear approach [21, 32]. As a statistical-based analytical method, response surface methodology (RSM) has been successfully employed to simultaneously evaluate the individual and combined effects of different engineering processes [5,17,24, 30,37]. The main advantage of the RSM method is that it requires fewer time-consuming experimental tests full factorial compared with design experimentation [25]. The literature review indicates that biochar could provide numerous advantages as a soil amendment [35] and a fuel additive in conventional diesel fuel [26]. However, the optimum condition of the pyrolysis process is not clear. Therefore, the main purpose of this study was to optimize the temperature/heating rate of biochar production processes through the pyrolysis of Prosopis farcta. And to our knowledge, this has not been done before. Also, the effect of independent variables (i.e., temperature (°C) and heating rate) were investigated on the response parameters (i.e., EC (ds/m), pH, SSA (m²/g), OC (%), and CEC (C mol/kg)).

2. Methodology and experimental setup

2.1. Study area

The present research was done in the city of Ahvaz, Khuzestan Province. In Ahvaz, *Prosopis farcta* is one of the dominant plant covers; therefore, its waste biomass can conveniently be used to produce biochar. The average temperature (2010-2020) and average annual precipitation in Ahvaz is 29°C and ~145 mm, respectively. According to the De Martonne [22], the study area is considered an arid climate.

2.2. Pyrolysis experiments

The obtained feedstocks were pyrolyzed at 400°C, 500°C, 600°C, 700°C, and 800°C for 3 h with a heating rate of 3°C/min, 4°C/min, 5°C/min, 6° C/min, and 7°C/min in a sealed reactor to prevent O₂ input (Muffle Furnace, SEF-101 Model). Then, the generated biochar was slowly cooled to room temperature to characterize.

2.3. Properties of Prosopis farcta

Prosopis farcta, as a species of the genus Prosopis, is mostly growing in the Middle East, for example, in Khuzestan Province, Iran. The higher classification of Prosopis farcta is Mesquites and belongs to the Family of Fabaceae. Moreover, it is a woody perennial legume shrub with 0.4-1 m high and a below-ground tree. This native species in Khuzestan has a strong and deep rooting system with branches going as deep as 20 m or more. This plant has high resistance against water stresses, and the leaves of Prosopis farcta are green-grey. Regarding the deep rooting system with a low level of water requirement, therefore, is a convenient option to conserve the soil against erosive factor.

2.4. Characterization of the biochar

In this study, after biochar production using standard methods, five effective parameters of biochar were recorded: electrical conductivity (EC), pH, specific surface area (SSA), cation exchange capacity (CEC), and organic carbon (OC). The SSA of the biochars was measured by the application of the Brunauer-Emmett-Teller (BET) model. Indeed the BET model is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption. The biochars' functional groups were identified by an FTIR spectrophotometer (Figure 1). Also, the electrical conductivity of biochar was measured in a 1:10 biochar: water ratio after 1 h of shaking on a reciprocating shaker at 25°C. After shaking, the samples were allowed to stand for 30 min, and then the EC was measured using a precalibrated EC meter in the laboratory [27]. In order to measure the pH of samples, the pH meter was calibrated using standard buffers of pH 7 and 10. The biochar pH was measured in a 1:5 biochar: water ratio after 1 h of shaking. Afterward, the samples were allowed to stand for 30 min, and pH was determined by a calomel electrode-glass electrode system [27, 28]. The cation exchange capacity of biochar was measured using ammonium acetate [23]. The OC was measured using the Walkley-Black method [34].



Fig. 1. The Fourier Transform Infrared (FTIR) analysis of biochar derived from *Prosopis farcta*.

3. Results and discussion

3.1. The effect of temperature/heating rate on EC

The results indicated a significant relationship between the input parameters (e.g., pyrolysis temperature and heating rate) and response variables, including EC, pH, SSA, OC, and CEC. According to the RSM findings, the quadratic model was found to be the best-fitted model to the experimental data, as shown in Table 1. The P-value of 0.0004 was achieved for EC variables, indicating a confidence interval of 95%. As can be seen in Table 1, the defined model was significant, illustrating the significant effect of independent variables of heating rate and temperature on the response factor of EC. Besides, the F-value of 92.56 shows that the derived model is statistically significant. The ANOVA analyses for the response surface quadratic model for electrical conductivity (EC) are reported in Table 1. The results show that for Factor-A (Temperature), the mean square (MS) is 2.26 and the F-value is 92.56; for the Factor-B (heating rate), the MS is 0.14, the F-value is 5.67,

and the p-value is 0.0487. The contour plot (2D) of the temperature/heating rate on the EC (Figure 2a), the 3D diagram of pyrolysis temperature, and the rate of heating on the EC of biochar (Figure 2b) are shown. As illustrated in Figure 1 and the statistical results (Table 1), the pyrolysis temperature/ heating rates were effective on the biochar EC. By enhancing the pyrolysis temperature and heating rate from 3° C to 7° C, the EC increased; the highest EC was achieved in the highest temperature of 800°C and the highest heating rate of 7°C/min. Furthermore, the results confirmed that pyrolysis temperature had a more substantial effect on biochar's structure than the heating rate. These results are inconsistent with Ahmad et al., who found that the EC of biochar augmented with increasing the pyrolysis temperature [2]. Awareness about the EC as soluble salts in the

biochar solution and the EC variability regarding the pyrolysis conditions is essential to determine the harmful effects of high concentration salts on plant growth [8]. Our results confirmed that temperature changing has a remarkable impact on the EC of biochar; therefore, it is necessary to consider the EC of the applied biochar to apply biochar as a soil amendment. To produce the biochar with the lowest EC, slow pyrolysis with the lowest temperature and the lowest heating rate is the best conditions. Generally, as a critical process parameter, temperature plays an important role in the thermal degradation of the pyrolysis process [31]. Also, Tamri et al. revealed that the heating rate of pyrolysis was effective on the molecular and structural characteristics of the produced biochar [31].

Table 1. The ANOVA ana	lysis for response surface	quadratic model for electrica	l conductivity (EC).

	Sum of		Mean Square	F-	p-value	
Source	Squares	Df		Value	Prob > F	
Model	2.70	5	0.54	22.14	0.0004	significant
A-temperature	2.26	1	2.26	92.56	< 0.0001	
B-rate	0.14	1	0.14	5.67	0.0487	
AB	6.250E-004	1	6.250E-004	0.026	0.8775	
A ²	0.30	1	0.30	12.33	0.0098	
B ²	0.041	1	0.041	1.67	0.2378	
Residual	0.17	7	0.024			



Fig. 2. The (a) contour plot of temperature and heating rate on EC, (b) the 3D diagram of pyrolysis temperature and the rate of heating on EC of biochar.

3.2. The effect of heating rate/temperature on pH

The statistical analysis of RSM parameters for pH demonstrates that pyrolysis factors, including temperature/heating rate, were significantly

effective on the pH of biochar. Also, regarding the statistical parameters, the quadratic model was suggested as the best model (Table 2). The contour plot of the temperature/rate on pH (Figure 3a), the 3D diagram of pyrolysis temperature, and the rate

of heating on pH of biochar (Figure 3b) are shown. As the results present, the pH of biochar increased by increasing the pyrolysis temperature/heating rate. Also, the F-value of 44.81 clearly indicates that the suggested model is statistically significant. The ANOVA analyses for the response surface quadratic model for pH are reported in Table 2. Moreover, for Factor-A (Temperature), the MS was 0.71, F-value was 177.29, and the p-value was <0.0001, and for Factor-B, the MS was 0.088, and F-value was 22.21. The results depicted a relation between EC and pH; by enhancing the pyrolysis temperature and heating rate, the EC and pH of biochar increased. The main reason was the effect of salts in the solution. In this regard, the results of other researches confirmed that the biochar pH was meaningfully enhanced with a higher pyrolysis temperature (P, 0.05). The results obtained were in agreement with those reported by Hossain et al., who found that the pH of the produced biochar was 10.2 at 400°C and 10.4 at 700°C, which confirmed the enhancing effect of the pyrolysis temperature on the biochar pH [7]. Furthermore, Zhao et al. stated that by increasing the pyrolysis temperature, the number of acidic functional groups, particularly the carboxylic group (-COOH), decreased [37]. And therefore, the biochar pH was enhanced. The primary functional groups increased with the enhancement of pyrolysis temperature, so the biochar pH increased [37]. The FTIR analysis clearly indicated the remarkable changes in functional groups in the biochar structure, and the main outcome of these changes was the changing of biochar pH. The pH variation is important and effective on biochar properties and reactions in the soil when applied to the soil as an organic amendment.

	Sum of		Mean	F-	p-value	
Source	Squares	Df	Square	Value	Prob > F	
Model	0.89	5	0.18	44.81	< 0.0001	significant
A-temp.	0.71	1	0.71	177.29	< 0.0001	
B-rate	0.088	1	0.088	22.21	0.0022	
AB	1.225E-003	1	1.225E-003	0.31	0.5963	
A ²	0.094	1	0.094	23.67	0.0018	
B ²	0.018	1	0.018	4.47	0.0723	
Residual	0.028	7	3.980E-003			





Fig. 3. The (a) contour plot of temperature and heating rate on pH, (b) the 3D diagram of pyrolysis temperature and the rate of heating on pH of biochar.

3.3. The effect of heating rate/temperature on SSA

The statistical analysis of the RSM parameters for SSA showed that pyrolysis factors, including heating rate/pyrolysis temperature, were effective parameters on the SSA of biochar. Also, the quadratic model was suggested as a best-derived model. Therefore, the quadratic model was fitted for SSA as a response in RSM (Table 3). As the results show, the p-value of <0.0001 and F-value of 35.36 confirm that the fitted model is significant. Therefore, it is capable of optimizing the pyrolysis conditions to determine the best biochar characteristics to manage the effectiveness of biochar in the soil as an organic amendment. Similarly, Waled Suliman et al. (2007) illustrated that the specific surface area of biochar was enhanced with the temperature of the pyrolysis process [33]. The contour plot of both the heating rate and temperature on the SSA and the 3D diagram of pyrolysis temperature and the rate of heating on the SSA of biochar are shown in Figure 4a and 4b, respectively. As the results show, by increasing the pyrolysis temperature and heating rate, the SSA of biochar increases. Moreover, the MS was 968.22, F-value was 130.31, and the p-value was <0.0001 for the A-factor (pyrolysis temperature). For B-factor (heating rate), the mean square (MS) was 58.48, the F-value was 7.87, and the p-value was 0.0263. Our results confirmed that generally, the effect of temperature on biochar characteristics was higher than the heating rate. For the specific surface area (SSA), the effect of the A and B factors was the same. The porous structure of biochar, which creates a high specific surface area [33] and high cation exchange capacity, help to enhance the capacity of treated soil to the formation of the complex with cationic heavy metal [14,15,16]. Also, other researches revealed that with enhancing the temperature of the pyrolysis process, the response parameters, including carbon content and the specific surface area, increased the pore volume of biochar [28,33]. Therefore, the structural

characteristics and behavior of biochar changed by changing the pyrolysis temperature. In addition, the aromaticity of biochar is a function of pyrolysis conditions, including pyrolysis temperature and heating rate. Indeed, by enhancing the pyrolysis temperature, the biochar aromaticity increases, which the outcome of this process could be the increment in specific surface area of biochar [2]. The higher pyrolysis temperature causes the lower biochar polarity; therefore, the pyrolysis conditions are effective on biochar characteristics. Lehmann et al. (2005) illustrated that pyrolysis conditions were effective on biochar structural characteristics [16]. Also, in this regard, the results of Keiluweit et al. (2010) confirmed that pyrolysis temperature significantly determined the pore size and sorptivity potential of produced biochar [9]. Moreover, the microstructure and surface chemistry of produced biochars meaningfully affect pyrolysis conditions [28]. By changing the pyrolysis temperature, the structural properties of biochar varied; therefore, the behavior of biochar as an amendment will be disparate. Previous studies confirmed that at the higher temperature, the pore volume of biochar was enhanced; thus, the SSA of biochar increased. Temperature variation can change the structural characteristics of produced biochar [37]. Also, similarly, the results of Shaaban et al. confirmed that the pyrolysis temperature due to the formation and volatilization of intermediate melts, as well as the release volatiles. affected of both the physical/chemical characteristics of biochar [29]. Indeed, one of the essential purposes of biochar production is its application as an organic amendment, so the structural characteristics are significant and deterministic regarding the biochar behavior in the soil. Therefore, it is essential to focus on the pyrolysis conditions in the biochar production process. The SSA parameter is very important and fundamentally influences the biochar characteristics. Consequently, the amount of this parameter should consider in the biochar production processes.

	Sum of		Mean	F-	p-value	
Source	Squares	Df	Square	Value	Prob > F	
Model	1313.75	5	262.75	35.36	< 0.0001	significant
A-temp.	968.22	1	968.22	130.31	< 0.0001	
B-rate	58.48	1	58.48	7.87	0.0263	
AB	9.27	1	9.27	1.25	0.3008	
A ²	236.83	1	236.83	31.88	0.0008	
B ²	3.12	1	3.12	0.42	0.5378	
Residual	52.01	7	7.43			

Table 3. The ANOVA analysis for response surface guadratic model for specific surface area (SSA).



Fig. 4. The (a) contour plot of temperature and heating rate on SSA, (b) the 3D diagram of pyrolysis temperature and the rate of heating on SSA of biochar.

3.4. The effect of heating rate/temperature on OC

In the present study, the input parameters showed a significant effect on the OC variables of biochar production parameters such as the heating rate and temperature of the pyrolysis process. As can be seen in Table 4, the quadratic model is the best model to predict the experimental results. The contour plot of temperature and heating rate on OC (Figure 5a) and the 3D diagram of pyrolysis temperature/the rate of heating on OC of biochar (Figure 5b) are shown. As the results show, by increasing the pyrolysis heating rate/temperature, the value of the OC of biochar increased. The results depicted that the mean square of the fitted model was 387.10, F-value was 25.35, and the pvalue was 0.0002 for the OC of biochar (Table 4). Also, for A-factor (pyrolysis temperature), the MS was 1604.45, F-value was 105.13, and the p-value was <0.0001. Therefore, the pyrolysis temperature

was effective on the amount of OC in the biochar. For the B-factor (heating rate), the MS was 44.54, F-value was 2.92, and the p-value was 0.1314, which highlights a significant effect of rate of heating on the biochar OC. According to the obtained results, by increasing pyrolysis temperature and heating rate, the OC of the produced biochar was enhanced; therefore, the highest OC was observed at the temperature of 800°C and the heating rate of 7°C/min, while the lowest OC was obtained at the pyrolysis temperature of 400°C and the heating rate of 3°C/min. Our results are inconsistent with Wu et al. They found that the temperature of pyrolysis had a remarkable effect on the amount of organic matter of the produced biochar, and the type of organic components regarding the pyrolysis temperature are disparate [36]. Therefore, it is essential to focus on pyrolysis temperature during the process of biochar production.

	/			J	· · ·	
	Sum of		Mean	F-	p-value	
Source	Squares	Df	Square	Value	Prob > F	
Model	1935.52	5	387.10	25.35	0.0002	significant
A-temp.	1605.45	1	1605.45	105.13	< 0.0001	
B-rate	44.54	1	44.54	2.92	0.1314	
AB	0.096	1	0.096	6.293E-003	0.9390	
A ²	283.58	1	283.58	18.57	0.0035	
B ²	12.10	1	12.10	0.79	0.4029	
Residual	106.90	7	15.27			

Table 4. The ANOVA analysis for response surface quadratic model for organic carbon (OC).



Fig. 5. The (a) contour plot of temperature and heating rate on OC, (b) the 3D diagram of pyrolysis temperature and the rate of heating on OC of biochar.

3.5. The effect of temperature/heating rate on CEC

According to the RSM results, the studied parameters, including the heating rate and temperature of the pyrolysis process, showed a significant influence on the CFC variable of biochar/biochar production factors. As shown in Table 5, the quadratic model was suggested as the best model to evaluate/predict the experimental value of the CFC data. The contour plot of temperature and rate on CEC (Figure 6a), the 3D diagram of temperature, and the rate of heating of the pyrolysis process on CEC of biochar (Figure 6b) are shown. The results showed that by increasing the pyrolysis temperature and heating rate, the CEC of biochar decreased. Indeed, our results showed that the effect of pyrolysis temperature and heating rate (Factor A and B) on the cation exchange capacity of produced biochar was different. As the contour plot (the 2D graph) showed, the trend of CEC changing with pyrolysis temperature is declining. The CEC of biochar changed from around 55 Cmole kg⁻¹ at 550°C to approximately 40 at 700°C (Figure 6a). Regarding the effectiveness of pyrolysis temperature on biochar CEC, Asif Naeem et al. (2016) showed that the pyrolysis temperature was effective on CEC. And by enhancing the temperature, the biochar CEC declined, and the highest CEC were observed at 500°C. The CEC of biochar influenced the activity and reactions of biochar in the soil, so it is essential to set the pyrolysis temperature during biochar production.

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	1577.85	5	315.57	52.90	< 0.0001	significant
A-temp.	1544.05	1	1544.05	258.82	< 0.0001	
B-rate	18.30	1	18.30	3.07	0.1233	
AB	0.22	1	0.22	0.037	0.8529	
A ²	7.07	1	7.07	1.19	0.3123	
B ²	3.96	1	3.96	0.66	0.4422	

Table 5. The ANOVA analysis for response surface auadratic model for cation exchange capacity (CEC)



Fig. 6. The (a) contour plot of temperature and heating rate on CEC, (b) the 3D diagram of pyrolysis temperature and the rate of heating on CEC of biochar.

3.6. RSM optimization and validation

A desirability function approach (DFA) was employed in this study to select the optimal value of pyrolysis conditions, e.g., heating rate and temperature. In the present study, the purpose of optimization was to maximize the marble powderto-cement ratio (M/C) and minimize the CEC characteristic of biochar. In this regard, the Design-Expert software version 10 was used to model/optimize the influence of temperature and the rate of heating in the pyrolysis process on the biochar characteristics. In the optimization process, the importance of all parameters was considered to be equal to three. Table 6 depicts the upper/lower boundary conditions, weight, and value of each response/input factor. According to the constraints mentioned above, the pyrolysis temperature of 700 °C and the heating rate of 6 were determined as optimal values, with higher desirability of 67%. The desirability value of each variable (e.g., input and response parameter) is illustrated in Figure 7. According to these optimized operating conditions, an EC of 2.58, pH of 10.9, SSA of 41.11, OC of 45.93, and CEC of 35 were obtained. Experimental validation was performed at the suggested conditions to test the accuracy of the obtained models. The difference between results predicted values experimental and indicated that RSM could successfully model and optimize the pyrolysis process, with an absolute error of less than 5%.

Factors	Goal	Upper limit	Lower limit	Upper weight	Lower weight	Importance
Heating rate	In range	6	4	1	1	3
Temperature	In range	700	500	1	1	3
EC	Maximize	3.19	1.48	1	1	3
pН	Maximize	11.28	10.23	1	1	3
SSA	Maximize	58.63	18.56	1	1	3
OC	Maximize	61.39	19.41	1	1	3
CEC	Minimize	72.89	29.34	1	1	3

Table 6. Optimization constraints.



Fig. 7. A graphical view of desirability value for each parameter.

4. Conclusions

In the present work, the chemical and structural characteristics of biochar derived from *Prosopis* pyrolysis farcta through conditions (i.e., temperature/rate of heating of the pyrolysis process) were evaluated. In conclusion, the effectiveness of the pyrolysis temperature was higher than the heating rate. The results indicated that the electrical conductivity, pH, specific surface area, and organic carbon of produced biochar were enhanced by increasing the temperature and heating rate. In contrast, the cation exchange capacity of biochar was decreased. Also, the enhancing pyrolysis temperature of the acidic functional groups declined. Regarding the optimization results using RSM, the pyrolysis temperature of 700 °C and heating rate of 6 were determined as optimal values, with higher desirability of 67%. The difference between the experimental results and predicted values indicated that RSM could successfully predict/optimize the pyrolysis process, with an absolute error of less than 5%.

Acknowledgment

We are grateful to the Research Council of Shahid Chamran University of Ahvaz for financial support (GN: 1323).

References

- Abbaspour, A., Asghari, H. R. (2019). Effect of biochar on nitrogen retention in soil under corn plant inoculated with arbuscular mycorrhizal fungi. Advances in environmental technology, 5(3), 133-140.
- [2] Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J. K., Yang, J. E., Ok, Y. S. (2012). Effects of pyrolysis temperature on soybean stover-and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresource* technology, 118, 536-544.
- [3] Naeem, M. A., Khalid, M., Ahmad, Z., Naveed, M. (2016). Low pyrolysis temperature biochar improves growth and nutrient availability of maize on typic calciargid. Communications in soil science and plant analysis, 47(1), 41-51.
- [4] Bridgwater, A. V., Carson, P., Coulson, M. (2007). A comparison of fast and slow pyrolysis liquids from mallee. *International journal of* global energy issues, 27(2), 204-216.
- [5] Daghaghele, S., Kiasat, A. R., Safieddin Ardebili, S. M., Mirzajani, R. (2021). Intensification of Extraction of Antioxidant Compounds from Moringa Oleifera Leaves Using Ultrasound-Assisted Approach: BBD-RSM Design. International journal of fruit science, 21(1), 693-705.
- [6] Dhaundiyal, A., Atsu, D., Toth, L. (2020). Physico-chemical assessment of torrefied Eurasian pinecones. *Biotechnology for biofuels*, 13(1), 1-20.

- [7] Hossain, M. K., Strezov, V., Chan, K. Y., Ziolkowski, A., Nelson, P. F. (2011). Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *Journal of environmental* management, 92(1), 223-228.
- [8] Joseph, S., Peacocke, C., Lehmann, J., Munroe, P. (2009). Developing a biochar classification and test methods. Biochar for environmental management: science and technology, 1, 107-126.
- [9] Keiluweit, M., Nico, P. S., Johnson, M. G., Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environmental science and technology, 44(4), 1247-1253.
- [10] Khademalrasoul, A., Naveed, M., Heckrath, G., Kumari, K. G. I. D., de Jonge, L. W., Elsgaard, L., Iversen, B. V. (2014). Biochar effects on soil aggregate properties under notill maize. *Soil science*, 179(6), 273-283.
- [11] Khademalrasoul, A., Kuhn, N. J., Elsgaard, L., Hu, Y., Iversen, B. V., Heckrath, G. (2019). Short-term effects of biochar application on soil loss during a rainfall-runoff simulation. *Soil* science, 184(1), 17-24.
- [12] Lehmann, J., Joseph, S. (2015). Biochar for environmental management: an introduction (pp. 33-46). Routledge.
- [13] Lehmann, J. and Joseph, S. (2009) Biochar for environmental management, Science and technology, pp. 405. London: Earthscan publishing.
- [14] Lehmann, J., da Silva, J. P., Steiner, C., Nehls, T., Zech, W., Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and soil*, 249(2), 343-357.
- [15] Lehmann, J., Gaunt, J., Rondon, M. (2006). Bio-char sequestration in terrestrial ecosystems-a review. Mitigation and adaptation strategies for global change, 11(2), 403-427.
- [16] Lehmann, J., Lan, Z., Hyland, C., Sato, S., Solomon, D. and Ketterings, Q. M. (2005) Long term dynamics of phosphorus and retention in manure amended soils. *Environmental science* and technology, 39 (17), 6672-6680.

- [17] Nematzadeh, M., Samimi, A., Shokrollahzadeh, S., Mohebbi-Kalhori, D. (2019). Bentazon removal from aqueous solution by reverse osmosis; optimization of effective parameters using response surface methodology. Advances in environmental technology, 5(4), 193-201.
- [18] Niebes, D., Schobel, S., Schneider, R., Schröder, D. (2001). Sprinkling experiments to characterize the influence of land coverage, land use and different soil types on runoff generation. In geophysical research abstracts (Vol. 3).
- [19] Novak, J. M., Busscher, W. J., Watts, D. W., Amonette, J. E., Ippolito, J. A., Lima, I. M., Schomberg, H. (2012). Biochars impact on soilmoisture storage in an ultisol and two aridisols. *Soil science*, 177(5), 310-320.
- [20] Ouyang, L., Wang, F., Tang, J., Yu, L., Zhang, R. (2013). Effects of biochar amendment on soil aggregates and hydraulic properties. Journal of soil science and plant nutrition, 13(4), 991-1002.
- [21] Pandian, M., Sivapirakasam, S. P., Udayakumar, M. (2011). Investigation on the effect of injection system parameters on performance and emission characteristics of a twin cylinder compression ignition direct injection engine fuelled with pongamia biodiesel-diesel blend using response surface methodology. Applied energy, 88(8), 2663-2676.
- [22] Pellicone, G., Caloiero, T., Guagliardi, I. (2019). The De Martonne aridity index in Calabria (Southern Italy). *Journal of mMaps*, 15(2), 788-796.
- [23] Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. R., Lehmann, J. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and fertility of soils*, 48(3), 271-284.
- [24] Ardebili, S. M. S., Solmaz, H., Calam, A., İpci, D. (2021). Modelling of performance, emission, and combustion of an HCCI engine fueled with fusel oil-diethylether fuel blends as a renewable fuel. *Fuel*, 290, 120017.
- [25] Ardebili, S. M. S., Solmaz, H., Mostafaei, M. (2019). Optimization of fusel oil–Gasoline blend

ratio to enhance the performance and reduce emissions. *Applied thermal engineering*, 148, 1334-1345.

- [26] Ardebili, S. M. S., Taghipoor, A., Solmaz, H., Mostafaei, M. (2020). The effect of nanobiochar on the performance and emissions of a diesel engine fueled with fusel oil-diesel fuel. *Fuel*, 268, 117356.
- [27] Singh, B., Dolk, M. M., Shen, Q., Camps-Arbestain, M. (2017). Biochar pH, electrical conductivity and liming potential. *Biochar: A* guide to analytical methods.
- [28] Singh, B., Singh, B. P., Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil* research, 48(7), 516-525.
- [29] Shaaban, A., Se, S. M., Dimin, M. F., Juoi, J. M., Husin, M. H. M., Mitan, N. M. M. (2014). Influence of heating temperature and holding time on biochars derived from rubber wood sawdust via slow pyrolysis. *Journal of analytical* and applied pyrolysis, 107, 31-39.
- [30] Solmaz, H., Ardebili, S. M. S., Calam, A., Yılmaz, E., İpci, D. (2021). Prediction of performance and exhaust emissions of a Cl engine fueled with multi-wall carbon nanotube doped biodiesel-diesel blends using response surface method. Energy, 227, 120518.
- [31] Tamri, Z., Yazdi, A. V., Haghighi, M. N., Abbas-Abadi, M. S., Heidarinasab, A. (2018). The effect of temperature, heating rate, initial cross-linking and zeolitic catalysts as key process and structural parameters on the degradation of natural rubber (NR) to produce

the valuable hydrocarbons. *Journal* of analytical and applied pyrolysis, 134, 35-42.

- [32] Vasseghian, Y. (2015). Modeling and optimization of oil refinery wastewater chemical oxygen demand removal in dissolved air flotation system by response surface methodology. Advances in environmental technology, 1(3), 129-135.
- [33] Suliman, W., Harsh, J. B., Abu-Lail, N. I., Fortuna, A. M., Dallmeyer, I., Garcia-Perez, M. (2016). Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. *Biomass and bioenergy*, 84, 37-48.
- [34] Walkley, A., Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil science, 37(1), 29-38.
- [35] Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., Chen, Y. (2012). Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and bioenergy*, 47, 268-276.
- [36] Wu, H., Qi, Y., Dong, L., Zhao, X., Liu, H. (2019). Revealing the impact of pyrolysis temperature on dissolved organic matter released from the biochar prepared from Typha orientalis. Chemosphere, 228, 264-270.
- [37] Zhao, L., Li, Q., Xu, X., Kong, W., Li, X., Su, Y., Gao, B. (2016). A novel Enteromorpha based hydrogel optimized with Box-Behnken response surface method: synthesis, characterization and swelling behaviors. *Chemical engineering journal*, 287, 537-544.