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Response of Fennel (*Foeniculum vulgare*) plants to the application of acidified biochar and its impact on phosphorus release utilizing kinetic models

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SOIL fertility and improvement of its properties depend on the fertilization process, which in turn affects nutrients release, especially phosphorus (P). The plant limitation to obtain an insufficient concentration of P is due to its fixation in primary and secondary minerals and/or its absorption on the organic materials surface. Finding an ideal formula or model is necessary to provide cross-validation between the experimental results and the empirical formula. In order to obtain the appropriate P availability, a suitable natural alternative must be found that uses the available resources. This study aims to investigate the impact of acidified biochar at two levels with 5 incubated times on phosphorus and carbon mineralization kinetic, as well as some soil chemical properties. Six equations (Zero-order, first- order, second-order, Elovich, power function, and parabolic diffusion model) was used to describe variations of released phosphorus and carbon mineralization with time. The results demonstrated that using acidified biochar decreased soil pH, increase organic matter and cumulative P release by time progress for all treatments. The acidified biochar caused a decline in the cumulative CO_2 emissions. Also, the addition of biochar had an encouraging impact on the development and vegetative growth of fennel plants. The best treatment that increased fresh weight, dry weight, and NPK uptake by fennel plants was BC_2. The Zero-order kinetic and parabolic diffusion models give better results with higher R^2 value. So, in order to create strategies for managing nutrients and soil carbon dioxide fluxes that contribute to climate change, it is crucial to consider the release kinetics and parameters associated with nutrient release and carbon mineralization from biochar.

Keywords: Release, Kinetics biochar, Calcareous soil, Crop yield.

1. Introduction

One of the most significant fragrant and medicinal plants, Fennel is grown as an annual and is ranked first among Egyptian exports of herbs and spices (Abu El-Leel and Yousef, 2017). As the harmful consequences of chemical fertilization become more widely known, the agricultural industry's primary goal is to provide safe agri-food products. Hegazi *et al.* (2023) discuss the use of substitutes for mineral NPK fertilizers while cultivating fennel for medicinal purposes. Though adding biochar to soil should improve plant nitrogen uptake efficiency, Egyptian soils and biochars are both alkaline (Khalil *et. al.*, 2023). The best solution, however, might be to add acidified biochar (Zang *et al.*, 2022). Although most crops contain plenty of both organic and inorganic phosphorous (P), it cannot be directly absorbed by living things. This because P is strongly reactive with some elements, it is only available to plants at extremely low concentrations (0.1% of the total P), where it is immobilized inside organic material, adsorbed to mineral surfaces, or locked within primary or secondary mineral particles (He *et al.*, 2023). It is urgent to find a different way that makes natural organic P resources more available for plants. Additionally, continued investigation and advancement in the field of nutrition may result in the creation of fresh strategies to improve phosphorus availability and optimize nutrient management techniques (El-Naqma *et. al.*, 2024). If crop leftovers are handled carefully, they can replenish soil organic matter, which is an important component in determining soil quality, and after mineralization, they provide essential plant nutrients (Ghosh *et al.*, 2023). Organic fertilizer can be made from various sources and methods, such as combining low-grade or acidified P with feed stocks that have been pyrolyzed under various pyrolysis conditions and then synthesizing biochar-based fertilizers (Lustosa Filho *et al.*, 2019). Around the

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world, and particular in Egypt, P availability is an important determinant for plant productivity, impacts climate change and atmospheric carbon dioxide (Hou *et al.,* 2020; Hou *et al.,* 2021; Ellsworth *et al.,* 2022; Cunha *et al.,* 2022). Comprehending the mechanism of soil organic carbon stabilization can facilitate the application of efficient management strategies aimed at retaining soil organic matter, enhancing soil structure, and diminishing greenhouse gas emissions (Singh *et. al.,* 2024).

To enhance sustainable soil phosphorus management, it is crucial to comprehend how a fertilizer regime affects the long-term accumulation and transformation of soil phosphorus. (Wang *et al.,* 2022). Phosphorus availability is frequently restricted by soil build up and it is insufficient. This made it necessary to find strategies for secondary phosphorus resource recovery and recycling (Schütze *et al.,* 2020). According to Hadgu *et al.* (2014), soil characteristics including amount of soil organic carbon, calcium carbonate and clay influence the rate at which phosphorus is released into soil solution to maintain its critical concentration (0.2 µg P m^{-1}).

Despite its high content, knowledge of the existing P forms in soil is crucial for its important role in crop growth (Yang *et al.,* 2021). The kinetics concept is one of the most promising strategies that predict and evaluate the state and chemistry of many nutrients, including phosphorus (Toor & Bahl 1999). Estimates of P release from soil related to time require understanding the rate of its reaction and kinetics. Therefore, many kinetic models have been developed to measure phosphorus release in soil, including first, second-order, energy function, equivalent diffusion and Elovitch equations (Abdu 2013). The behavior of the continuous interactions between various ions in the soil solution and the solid phase over time must be defined using the kinetics concept, and the release of phosphorus and nitrogen from the soil can be better visualized using the thermodynamic and dynamics concepts. Our hypothesis is based on producing acidified biochar (ABC) derived from fish waste P-rich, as an alternative source to phosphate as a chemical fertilizer which may increase P availability as slow release with time and enhance Fennel plants growth. The aims of the current study i) assess the impact of acidified biochar at different rates and incubation periods on soil properties and Fennel plants growth, ii) evaluate the kinetic models describing P release rate from calcareous soils and iii) tracking changes in P release impacted by biochar addition at different pyrolysis temperatures.

2. Materials and Methods

2.1 Soil and Biochar

Thirty km away from the eastern Assiut province, Egypt, surface soil samples (0-30cm) were randomly collected from the Experimental Farm, Agric. Res. Station, Arab Al Awamer (27°12′ 16.67′ N latitude and 31°09′ 36.86′ E longitude). The collected samples were, well mixed air-dried, sieved with a 2 mm sieve to be ready for the experiment and analysis. The chemical and physical properties were analyzed based on Page (1982) and Klute (1986) and they are shown in table (1).

Table 1. Some chemical and physical properties of the tested soil.

Property	Unit	Value
Sand	(g/kg)	877
Silt	(g/kg)	82
Clay	(g/kg)	41
Texture	-	Sandy
Soil pH (1: 2.5)	-	8.42
Soil EC (1: 2.5)	(dS/m)	0.39
Organic matter	(g/kg)	3.50
Available-N	(mg/kg)	10.3
Available-P	(mg/kg)	3.16
Available-K	(mg/kg)	53.00
$CaCO_3$	(g/kg)	110

From Al-Sharq Company for feed, Quesna, Menoufia Governorate, Egypt, raw materials of fish wastes (viscera, head, and bones) as a powder were obtained and pyrolyzed at 400 and 600 ^{0}C. To increase P content, the biochar (derived from fish waste) was mixed well with a fine rock phosphate (14.52% P, 33% P_2O_5) at a ratio of 95 biochar: 5 rock phosphate (W/W) to form a homogeneous mixture.

In order to imitate the production of superphosphate, concentrated H_2SO_4 was added to the biochar-rock phosphate combination at a 1:1 ratio, and the mixture was vigorously agitated for twelve hours using an electric stirrer. Then the acidified mixture was crushed one more and sieved using a 0.80 mm sieve after being air dried for 12 hours and oven dried for two hours at 105 ^{o}C. Table (2) presents the chemical properties of acidified biochar.

Table 2. Some chemical properties of the used acidified biochar.

Property	Unit	Biochar at 400 °C	Biochar at 600 °C
pH (1: 2.5)	---	4.4	4.8
Electrical conductivity (EC)	(dS/m)	8.34	8.86
Organic matter (OM)	(g/kg)	540	528
Available-N	(g/kg)	6.67	6.41
Available-P	(g/kg)	9.13	9.08
Available-K	(g/kg)	2.32	2.45
Total-N	(g/kg)	43	40
Total-P	(g/kg)	51	45
Total-K	(g/kg)	17	19

2.2 Incubation experiment

An incubation experiment was conducted in the winter season, 2020 using airtight plastic containers, 50 g of air-dried soil samples and mixed well with a tested material were placed in plastic cups. The pyrolyzed material at 400 and 600 ^{0}C with two rates (1 and 2%) was added. In addition, recommended dose of super phosphate (12%) was used compared to without biochar and fertilizer (control). So, the treatments were: 1) Control without any biochar or fertilizers (CK), 2) Recommended rate of superphosphate 12% (CF), 3) 1% B-400 ^{0}C (BC_1), 4) 2 % B-400 ^{0}C (BC_2), 5) 1% B-600 ^{0}C (BC_3) and 6) 2% B-600 ^{0}C (BC_4) as shown in Fig. (1).

All treatments were subjected to five incubation durations (2, 15, 30, 60 and 100 days) that applied to each treatment; all in a laboratory were kept at 25–30 ^{0}C. A total of 90 experimental units were formed by grouping the treatments into randomized block designs with three replications. Weekly checks and adjustments were made to the moisture level of the treatments, which had been wetted to the field capacity. At the end of each incubation period, the emitted carbon dioxide (CO_2) was trapped in NaOH solution and then determined using the back titration method of the excess NaOH with a dilute hydrochloric acid (Hopkins 2008). Also, soil samples were taken to measure soil electrical conductivity (EC) was determined using a conductivity meter and pH by a digital pH meter in 1:2.5 (soil/water) suspensions (Rhoades 1996). The organic matter was determined using the Walkly-Black method; the available P was determined by the molybdenum blue colorimetric method (Murphy & Riley 1962) after extraction by 0.5 M $NaHCO_3$ (Olsen *et al.,* 1954).

2.3 Kinetics of phosphorus release and carbon mineralization

Using the Lavenberg-Marquardt and linear methods, the best fit model was identified to explain the quantity of P release and soil carbon residue lost during the incubation time, which in turn computes the kinetic parameter. Phosphorus release and carbon emission data were fitted to six different models following equations as shown in Table (3). Each kinetic model was tested by coefficient of determination (R^2) and the standard error of estimate (S.E.), calculated in SPSS 16.0 (Suwanree *et. al.,* 2022).

Table 3. Kinetics models fitted to P release and carbon mineralization versus time data.

Model	Equation	Parameter
Zero order	$C_A = C_{A0} + k_A t$	k_A is rate coefficient
First order	$\ln C_A = \ln C_{Ao} + k_A t$	k_A is first-order rate coefficient
Second order	$1/C_A = 1/C_{A0} + k_A t$	k_A is second-order rate coefficient
Power function	$\text{Ln } C_A = \ln k_A + b \ln t$	k_A is rate coefficient and b is empirical constant
Elovich	$C_A = (1/\beta)1n(\alpha\beta) + (1/\beta)\ 1n\ t)$	α is initial P release rate coefficient and β is release constant
Parabolic diffusion	$CA = Rt^{1/2} + C$	R is diffusion rate constant

2.3 Pot experiment

The plastic pots diameter 15 cm × height 25 cm were filled with 4 kg from the air-dried soil mixed well and with the tested material according to the concentrations and mixing ratios of modified biochar that mentioned previously which were used in the incubation experiment, so that the mixture was homogeneous and distributed randomly. Fennel-Baladi variety (*Foeniculum vulgare*) was selected as a winter crop, which was planted on 15th October, 2020 with 6 seeds per pot, and then it was thinned to two plants per pot after two weeks from planting. The recommended fertilizer doses of nitrogen (N) as ammonium nitrate (33.5%) at rate of 290.5 kg ha^{-1} and potassium (K) in the form of potassium sulfate (48%) at rate 119 kg ha^{-1}, respectively were added. Two equal doses of the nitrogen fertilizer were added; the first dose was added at 30 days after planting (DAP) and the second dose 45 DAP, while the K fertilizer was added as a single dose 30 DAP. The plants were irrigated when the soil moisture content adjustment at 70% of field capacity. The experiment was continued in the greenhouse condition until the maturity stage. The growth parameters such as fresh and dry weight were recorded. Plant samples were taken at the experiment end after 100 days; the plant sample was ground kept for chemical analyzes. Using H_2SO_4-$HClO_4$ acid mixture, the total content of the nitrogen, phosphorus and potassium nutrients in the plant material was estimated According to (Zarcinas *et al.*, 1987).

2.4 Statistical analyses

The significance differences among the treatments was examined using the Duncan multiple range tests at a 5% level of probability and the analysis of variance a one-way-ANOVA. Costat software was used to undertake statistical analyses of the data. (Steel & Torrie, 1986).

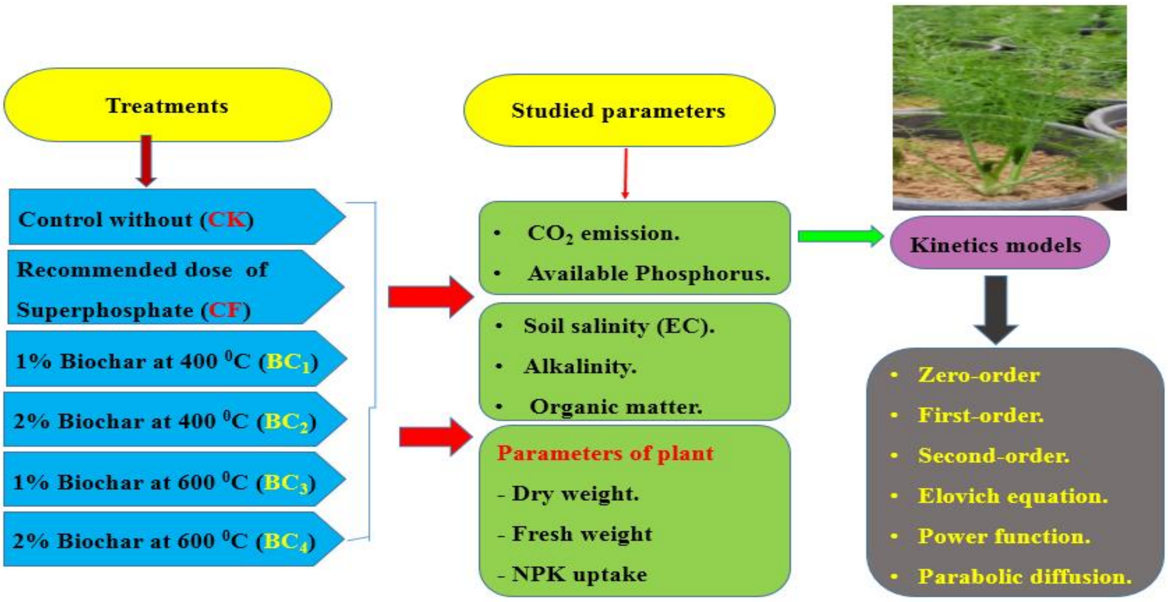

Fig. 1. General description of the research paper.

3. Results

3.1 Soil properties

The influence of acidified biochars and their rates through incubation experiment at different periods on the soil pH (average values) is illustrated in Table (3). It is observed that the soil pH as affected by pyrolyzed biochar at 400 ^{0}C is less than that of 600 ^{0}C regardless the incubation periods. Also, increasing the application rate of the acidified biochar led to obvious decrease in the soil pH regardless the pyrolysis temperature. In general, regarding the incubation periods, soil pH showed a minimum value after 15 and 30 days for all biochar addition rates. While it realized a maximum value after 2 days for 1% rate regardless pyrolysis temperature. Calcareous soil pH values lowered from 8.41 for CK treatment to 8.19, 7.51, 7.47, 7.59, and 7.53 for CF, BC_1, BC_2, BC_3, and BC_4 treatments, respectively, after applying acidified biochar through 100 days incubation period. Data in Table (3) indicated that the addition of acidified biochars caused a significant increase ($p<0.05$) in soil salinity (EC) compared to the control treatment. Regular increases of EC with biochar rates and the incubation period were noticed. After 2-day incubation, EC increased by 16.67, 62.50, 170.83, 68.75 and 131.25.83% for CF, BC_1, BC_2, BC_3, and BC_4 treatments, respectively, compared to the control (CK). While after 100 days, it increased by 58.0, 150.0, 304.0, 168.0 and 244.0% for CF, BC_1, BC_2, BC_3, and BC_4 treatments, respectively, compared to the control one (CK).

Table 3. Effect of acidified biochar at different pyrolysis temperature and their rate on soil properties.

Treatments	Days of incubation				
	2	15	30	60	100
			Soil pH (1:2.5)		
CK	8.44±0.05	8.40±0.03	8.40±0.03	8.41±0.05	8.41±0.02
CF	8.37±0.04	8.32±0.04	8.18±0.02	8.21±0.07	8.19±0.01
BC_1	7.62±0.03	7.37±0.02	7.36±0.04	7.49±0.02	7.51±0.04
BC_2	7.36±0.03	7.20±0.02	7.17±0.02	7.42±0.04	7.47±0.03
BC_3	7.68±0.04	7.41±0.03	7.41±0.02	7.51±0.03	7.59±0.04
BC_4	7.39±0.03	7.22±0.03	7.23±0.02	7.46±0.04	7.53±0.05
		Soil EC (1:2.5) dS m^{-1}			
CK	0.48±0.03e	0.49±0.02d	0.50±0.04e	0.48±0.05d	0.50±0.03e
CF	0.56±0.04d	0.61±0.02c	0.67±0.03d	0.74±0.05c	0.79±0.02d
BC_1	0.78±0.03c	0.85±0.03b	0.98±0.04c	1.13±0.06b	1.25±0.04c
BC_2	1.02±0.06b	1.21±0.05a	1.33±0.04b	1.54±0.06a	1.68±0.06a
BC_3	0.81±0.02c	0.87±0.04b	1.05±0.08c	1.19±0.05b	1.34±0.03b
BC_4	1.11±0.04a	1.24±0.07a	1.42±0.03a	1.64±0.05a	1.72±0.05a
		Soil O.M (g kg^{-1})			
CK	3.52±0.04e	3.55±0.06f	3.57±0.04f	3.63±0.07f	3.69±0.03f
CF	3.68±0.06d	3.77±0.05e	3.97±0.09e	4.12±0.04e	4.17±0.04e
BC_1	5.24±0.04c	6.38±0.02c	8.21±0.13c	9.15±0.06c	9.68±0.04c
BC_2	6.17±0.08a	8.03±0.08a	9.81±0.14a	11.15±0.06a	12.33±0.07a
BC_3	5.11±0.03c	5.99±0.18d	7.69±0.16d	8.39±0.07d	9.29±0.03d
BC_4	5.98±0.01b	7.84±0.05b	9.48±0.09b	10.96±0.08b	11.98±0.08b

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD, n = 10) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

Also, it is observed that the soil EC values resulted from biochar pyrolyzed at 400 ^{0}C are less than those at 600 ^{0}C regardless addition levels or incubation periods. The organic matter values (Table 3) significantly increased with increasing the biochar levels under all incubation periods. The organic matter values after 2-day incubation ranged from 5.11 to 5.24 g kg^{-1} and from 5.98 to 6.17 g kg^{-1} for 1% and 2% treatments, respectively regardless of the pyrolysis temperatures. Organic matter (OM) values gradually increased with increasing biochar amounts for BC_1, BC_2, BC_3, and BC_4, compared to CK treatment during a 100-day incubation period. These values were 3.69, 4.17, 9.68, 12.33, 9.29 and 11.98 g kg^{-1} for CK, CF, BC_1, BC_2, BC_3 and BC_4 treatments, respectively. Overall, the highest organic matter values were observed with biochar pyrolyzed at 400 ^{0}C for all incubation periods.

3.2 Phosphorus release

The effect of acidified biochar pyrolyzed at 400 and 600 ºC at different levels on the cumulative P release is shown in Fig. (2). The cumulative P release ranged from 3.64 to 19.67 and from 3.54 to 19.45 mg kg^{-1} for biochar pyrolyzed at 400 and 600 ^{0}C respectively, regardless the incubation period or addition level. Compared to other treatments, the highest value of cumulative P release (19.67 mg kg^{-1}) was recorded with BC_2 treatment after 100-days incubation period. While the lowest one (3.13 mg kg^{-1}) was observed with CK treatment at 2-days incubation period. Also, almost similar results are recognized for daily rate of P release (Fig. 3). The data showed that adding acidified biochar to tested soil significantly increased the daily rate of P release compared to the untreated one. Generally, the results showed that the daily rate of phosphorus release results from BC-600 treatments are less than that resulted from BC-400 regardless addition rate. The rate of P release from control (CK) and recommended P dose (CF) treatments is less than that resulted from all biochar treatments. The daily rate of P release increased significantly with increasing biochar levels during all incubation periods. Regarding the incubation periods, the results indicated that the lowest value was observed at 100-day period, while the highest values were noticed at 2 days. The daily rate of P release ranged between 1.77 to 1.82 and 1.95 to 2.01 mg kg^{-1} d^{-1} at levels of 1 and 2%, respectively, for all treatments regardless pyrolysis temperatures (400-600 ^{0}C) after 2-day incubation. After 100-days incubation, the rate of P release ranged from 0.14 and from 0.19 to 0.20 mg C kg^{-1} soil d-1 at levels 1 and 2%, respectively, for all treatments regardless pyrolysis temperatures. However, among incubation periods, the daily rate of P release was numerically in the order of 100-day < 30-day < 60-day < 15-day < 2-day.

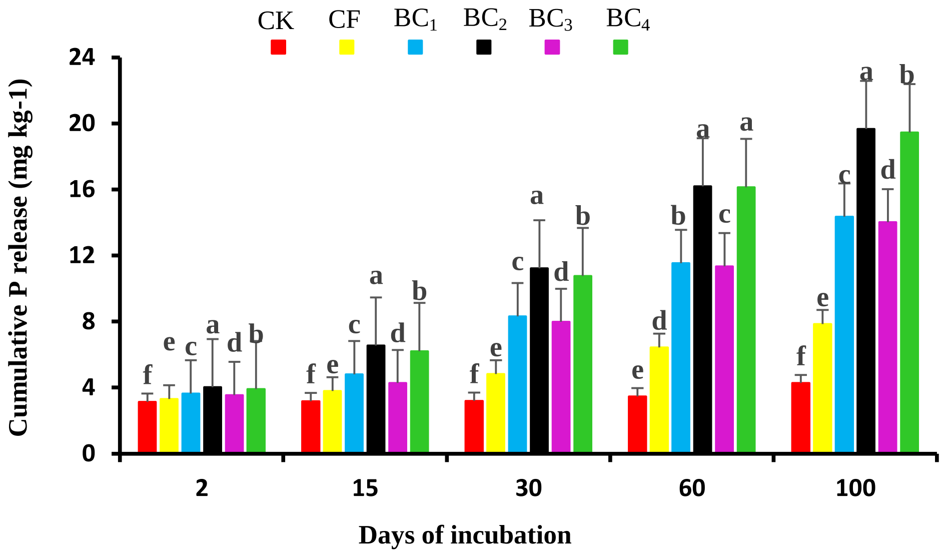

Fig. 2. Effect of acidified biochar at different rates and pyrolysis temperature on cumulative P release under incubation periods.

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

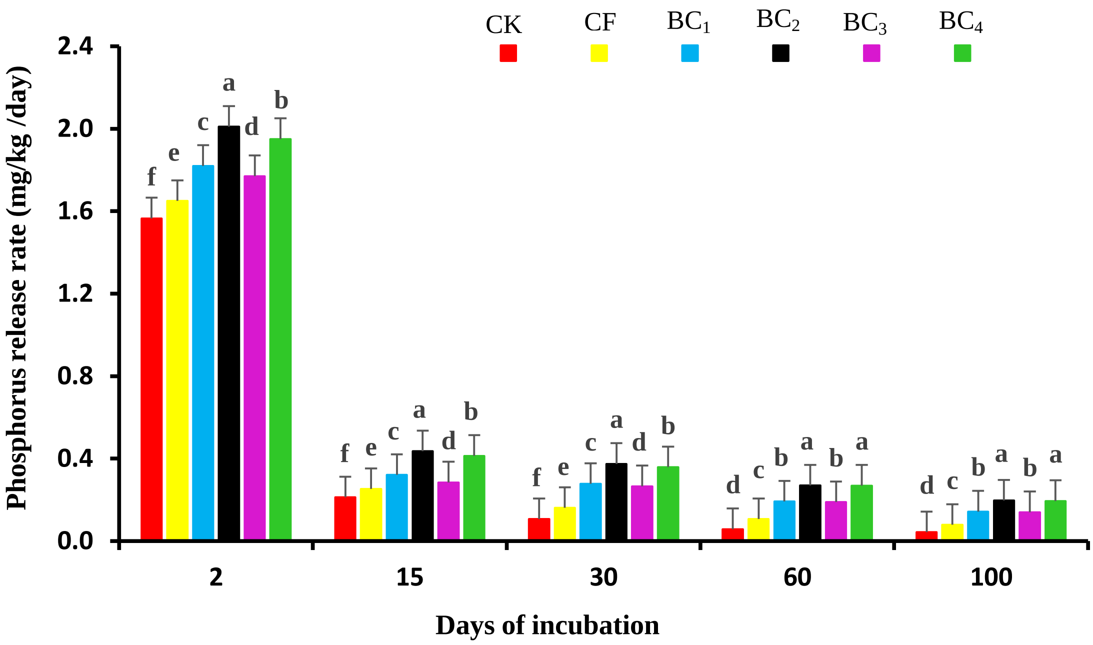

Fig. 3. Daily rate of P release in relation to biochar application at different rates during different incubation periods.

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

3.3 Kinetic equations of P release

Developing a mathematical model is necessary to provide a quantitative explanation of the P release mechanism. Finding the perfect formula or model is essential to providing mutual validation between the experimental results and the empirical formula. The P release and its time in amended soils by biochar can be described using the kinetic equations (Zero-order, first-order equation, second-order equation, Elovich equation, power function, and parabolic diffusion model). All six models generally fit the experimental data well; Table (4) displays standard errors of estimation (S.E.) and coefficients of determination (R^2) for the kinetic equations that were evaluated to explain the phosphorus release data, and table (5) displays the rate constants that resulted from these equations.

Table 4. Coefficients of determination (R^2) and standard errors (S.E) for the kinetic equations used to describe the kinetic release of phosphorus during incubation periods from calcareous soil.

Treatments	Zero order		First order		Second order		Elovich		Power function		Parabolic diffusion	
	R^2	S.E	R^2	S.E	R^2	S.E	R^2	S.E	R^2	S.E	R^2	S.E
CK	0.893	0.214	0.909	0.581	0.925	0.159	0.490	0.124	0.512	0.581	0.736	0.214
CF	0.987	0.845	0.957	0.161	0.906	0.033	0.788	0.845	0.855	0.161	0.963	0.845
BC_1	0.958	2.01	0.879	0.259	0.771	0.389	0.828	2.010	0.903	0.259	0.970	2.010
BC_2	0.949	2.91	0.845	0.293	0.697	0.366	0.862	2.010	0.952	0.293	0.981	2.910
BC_3	0.953	2.01	0.876	0.268	0.780	0.417	0.803	2.010	0.865	0.268	0.957	2.010
BC_4	0.950	2.92	0.853	0.299	0.709	0.381	0.849	2.910	0.943	0.299	0.976	2.920

CK = control without, CF = recommended dose of superphosphate 12%, BC_1=1% Biochar at 400 ^{0}C, BC_2= 2 % Biochar at 400 ^{0}C, BC_3= 1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C.

Table 5. Kinetic parameters of the selected equations describing the kinetic release of phosphorus in studied soil.

Treatments	Zero order	First order	Second order	Elovich		Power function		Parabolic diffusion
	K_0	K_1	K_2	α	β	A	B	k_p
CK	0.01152	0.00310	-0.00087	63900	4.550	0.06097	2.830	0.1231
CF	0.04783	0.00896	-0.00177	5.790	0.909	0.21812	2.530	0.5563
BC_1	0.11208	0.01380	-.0.00195	2.910	0.373	0.36059	2.460	1.3276
BC_2	0.16150	0.01530	-0.00174	3.270	0.252	0.41889	2.700	1.9335
BC_3	0.11185	0.01430	-0.00210	2.680	0.378	0.36582	2.310	1.3195
BC_4	0.16237	0.01570	-0.00183	3.100	0.253	0.42543	2.570	1.9379

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C.

Phosphorus release was best described by Zero order and Parabolic diffusion as judged by higher coefficient of determination (R^2 = 0.89- 0.99 for Zero order and R^2 = 0.74- 0.98 for Parabolic diffusion) followed by first order (R^2 = 0.85-96), Power function (R^2=0.51-0.95), second order (R^2=0.70-0.93) and the Elovich was the lower one (R^2= 0.49-0.86). Values of Elovich constants α and β varied with CK and CF treatments compared to biochar treatments, also these constants varied with addition levels. Where a high rate value (α) and a low constant value (β) signifies faster release kinetics. The chemical fertilizers (CF) treatment would have the fastest release kinetics compared to biochar treatments. Likewise, the release constants for Parabolic diffusion equation (k_p) and power function (a and b), varied with biochar treatments compared to CK and CF treatment. They showed linear increase with addition biochar and levels. The second order similarly fit the experimental data; the slope (k_2)

indicated that extractability decreases with time and has a negative value, signifying the rate at which P is supplemented from the soil solid phase as a result of the soil solution's decreasing P concentration.

3.4 Carbon dioxide emissions (CO_2)

The acidified biochar applying to tested soil, showed that, the daily rate of CO_2 emission was significantly lower than it was for treatment CK in Fig (4). In general, the data indicated that the daily rate of soil CO_2 emission results from BC-400 treatments is less than that resulted from BC-600 regardless addition level. The soil CO_2 emission rate from control (CK) and recommended dose P (CF) treatments is higher than that resulted from all biochar treatments. The rate CO_2 emission decreased significantly with increasing biochar levels during different incubation periods. While the highest values were noticed at 2 days, the lowest value was observed at 15-day period then gradually increased. After 2-day incubation, the daily rate of soil CO_2 flux ranged between 10.0 to 11.0 and 8.00 mg C kg^{-1} soil d^{-1} at levels of 1 and 2%, respectively, for all treatments regardless pyrolysis temperatures (400-600 ^{0}C). The corresponding values after 100-days incubation ranged from 2.06 to 2.10 and from 1.88 to 1.92 mg C kg^{-1} soil d^{-1} at levels 1 and 2%, respectively. However, among incubation periods, the rate of CO_2 emission was numerically in the order of 100-day < 30-day < 60-day < 15-day < 2-day.

Also, almost similar results are recognized for cumulative CO_2 (Fig. 5). The amount of cumulative CO_2 from control (CK) treatment was the highest one during all incubation periods compared to biochar treatments. Also, the cumulative CO_2 values were significantly ($p < 0.05$) decreased in all biochar treatments than other treatments. The decreases were varied according to biochar level and pyrolysis temperature as well as different incubation periods. The cumulative CO_2 values resulted from the biochar at 400 ^{o}C were lower than those resulted from biochar at 600 ^{o}C. The cumulative CO_2 ranged from 16.0 to 206.0 and from 16.0 to 210.0 (mg c kg^{-1}soil) for BC_{400} and BC_{600} treatments, respectively, regardless incubation period or addition level. The lowest values (16.0 mg c kg^{-1} soil) were observed with BC_2 and BC_4 at 2-day of incubation period. While it heading towards gradually increase via incubation time which was the highest (210.0 mg c kg^{-1}soil) one with treatment BC_3 at 100-day.

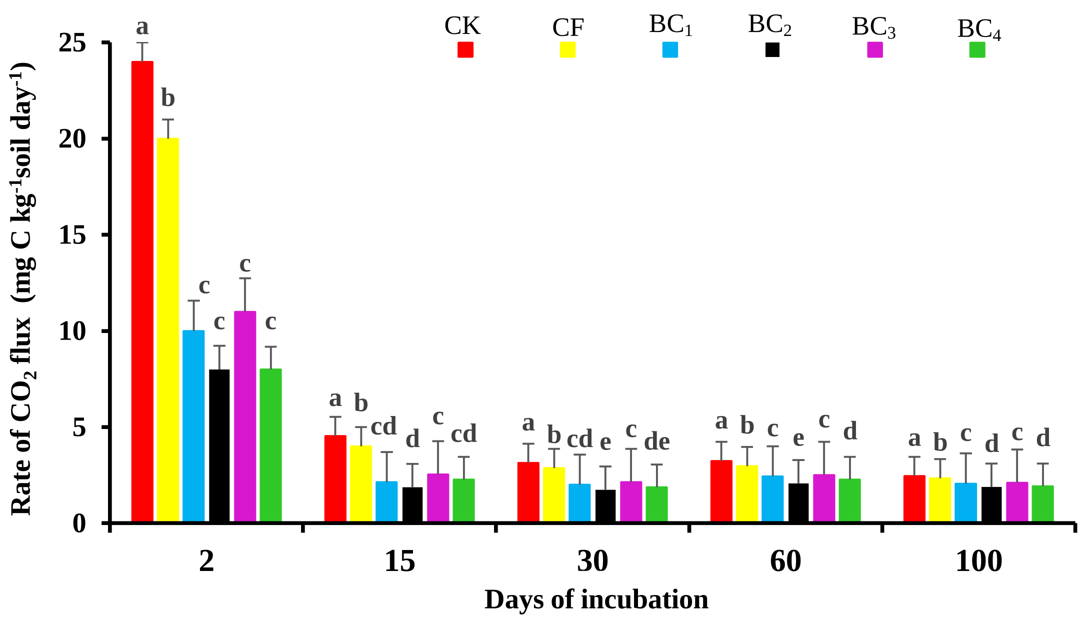

Fig. 4. Daily rate of CO_2 flux in relation to biochar application at different rates during incubation periods.

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

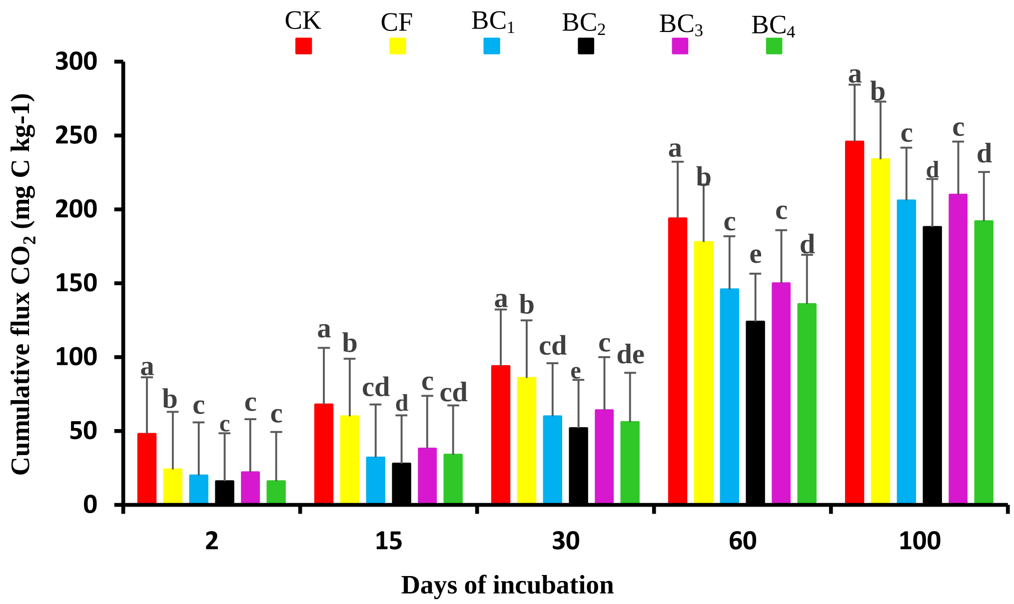

Fig. 5. Influence of acidified biochar on cumulative CO_2 flux in calcareous soil.

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

3.5 Kinetic equations of carbon mineralization

The kinetics of carbon mineralization of two forms of acidified biochar and its rates were investigated by testing six equations in the studied soil. In general, the six models all fit to describe the carbon mineralization kinetic quite well. The value of the determination factor (R^2) determines which model is deemed appropriate for the supplied data based on the measures associated with each equation.

Table 6. Kinetic parameters and R^2 of the Zero, First and Second-order describing the kinetic of carbon mineralization from calcareous soil.

Treatments	Zero-order			First-order			Second-order		
	Q_e	K_0	R^2	Q_e	K_1	R^2	Q_e	K_2	R^2
CK	40.83	2.15	0.97	53.33	0.0170	0.93	56.26	-0.00016	0.84
CF	25.57	2.19	0.98	36.08	0.0214	0.86	35.13	-0.0004	0.61
BC_1	8.98	2.02	0.98	23.90	0.0241	0.93	2.50	-0.000418	0.76
BC_2	5.24	1.84	0.99	19.80	0.0250	0.93	21.09	-0.000514	0.73
BC_3	12.80	2.03	0.98	27.09	0.0229	0.92	28.60	-0.000367	0.74
BC_4	8.73	1.89	0.99	21.81	0.0246	0.91	22.40	-0.000487	0.67

CK = control without, CF = recommended dose of superphosphate 12%, BC_1=1% Biochar at 400 ^{0}C, BC_2= 2 %Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C.

Table 7. Kinetic parameters and R^2 of the Elovich, Power function and Parabolic diffusion equations describing the kinetic of carbon mineralization.

Treatments	Elovich			Power function			Parabolic diffusion	
	α	β	R^2	A	b	R^2	k_p	R^2
CK	30.21	0.0207	0.74	0.4211	20.29	0.86	24.81	0.93
CF	20.25	0.0196	0.80	0.5858	10.42	0.97	25.60	0.96
BC_1	10.62	0.0225	0.71	0.6061	9.92	0.88	23.09	0.92
BC_2	10.38	0.0250	0.71	0.6326	7.86	0.90	20.93	0.92
BC_3	10.75	0.0223	0.72	0.5822	10.15	0.90	23.20	0.93
BC_4	10.50	0.0239	0.73	0.6401	8.28	0.93	21.60	0.93

CK = control without, CF = recommended dose of superphosphate 12%, BC_1= 1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C.

The data in tables (6 & 7) indicates that the Zero-order, first-order and second-order kinetic models were fitting for carbon mineralization. The data showed that R^2 was 0.97–0.99 and 0.92 -0.96 for Zero-order and Parabolic diffusion kinetic models, respectively, which can describe variations of carbon mineralization better than the other models. Both k_0 and Q_{e-0} were regular decrease with increasing the biochar levels which indicates that the carbon mineralization can be low with biochar increases compared to the control. Also, Q_{e-0} of CK treatment is the most followed by Q_{e-0} of CF treatment while the lowest values of Q_{e-0} were observed with biochar treatments. In addition, according to parameters of Parabolic diffusion model in Table (7), the k_p is obviously higher with CK CF treatments than biochar treatments, which means the process of carbon mineralization from biochar is mainly slow phase. Similarly, the carbon mineralization constants for power function (a & b), varied with biochar treatments compared to CK and CF treatment.

3.6 Effect of biochar on growth parameters and NPK uptake of Fennel-Baladi plant

Data presented in table (8) showed that the fresh, dry weight and nutrients uptake of the fennel plants were affected by biochar application. All treatments were increased the fresh, dry weight and NPK uptake than the control treatment.

Table 8. Effects of biochar application at different rates and pyrolysis temperature on fresh, dry weight and nutrients uptake by Fennel-Baladi.

Treatments	Fresh weight (g)	Dry weight (g)	Uptake (g pot^{-1})		
			N	P	K
CK	8.97±0.36^{d}	1.67±0.16^{e}	0.58±0.09^{d}	0.31±0.03^{d}	0.72±0.08^{d}
CF	14.56±0.18^{c}	3.50±0.28^{d}	1.54±0.22^{c}	1.13±0.49^{c}	1.95±0.11^{c}
BC_1	24.38±0.45^{b}	5.14±0.18^{bc}	4.02±0.32^{b}	3.43±0.20^{b}	5.04±0.39^{b}
BC_2	29.16±0.23^{a}	5.98±0.26^{a}	5.58±0.26^{a}	4.91±0.44^{a}	7.17±0.71^{a}
BC_3	23.75±1.36^{b}	5.07±0.23^{c}	3.98±0.13^{b}	3.39±0.51^{b}	4.84±0.33^{b}
BC_4	28.13±0.42^{a}	5.51±0.15^{b}	5.55±0.23^{a}	4.42±0.22^{a}	7.04±0.09^{a}

CK = control without, CF = recommended dose of superphosphate 12%, BC_1=1% Biochar at 400 ^{0}C, BC_2= 2% Biochar at 400 ^{0}C, BC_3=1% Biochar at 600 ^{0}C, BC_4= 2% Biochar at 600 ^{0}C. Means (± SD, n = 10) denoted by the same letter indicate insignificant difference according to Duncan's test at $p < 0.05$.

Among these treatments, the superior treatment that gives the highest increase in fresh, dry weight and NPK uptake by fennel plants was biochar 400 ^{0}C (BC_2) than other treatments. Applying 2% of the biochar at 400 ^{o}C (BC_2) increased the fresh and dry weight by 225.08 and 258.1% respectively, over the control. In general, data indicated that the amount of phosphorus uptake increased from 1.13 g pot^{-1} in case of chemical fertilizers (CF) to 3.43 and 4.91 g pot^{-1} for biochar at 400 ^{0}C (BC_1) and (BC_2), respectively compared to the control. While it increased to 3.39 and 4.42 g pot^{-1} for biochar at 600 ^{0}C (BC_3), and (BC_4), respectively.

4. Discussion

4.1 Soil properties

Acidified biochar significantly ($P < 0.05$) decreased soil pH and increased soil EC, and soil organic matter (SOM). It is worthy to note that a substantial decrease in soil pH was obviously with increasing the addition level (Table 3). Since cellulose degradation produce organic acids and phenolic compounds that lower the pH values (Zhang *et al.*, 2021). Similar results were reported by Karimi *et al.*, (2020) whom revealed that adding different levels of acidified biochar resulting from low-temperature pyrolysis to calcareous soil resulted in lowering soil pH. In addition to organic acids resulting from cellulose decomposition, an increase in acidic functional groups on the biochar surface has been suggested as a reason for the decrease the soil pH (Al-Wabel 2019). The electrical conductivity (EC) values depend on the pyrolysis temperature and the types of biochar raw materials used (Amin 2022). The results of other studies using biochar showed higher electrical conductivity values with increasing its rate due to it contains soluble salts of basic cations (Rekaby *et al.*, 2021). Also, the increase in soil organic matter (Table 3) depends on the soil pH, biochar properties, its organic matter concentration, its addition rate, and incubation periods (Sun *et al.*, 2022). The porous biochar structure can also increase the stability of soil organic carbon against biodegradation, thus reducing its mineralization rate (Liu *et al.*, 2019).

4.2 Cumulative P and Kinetics of P release

Biochar can affect phosphorus availability directly by changing soil pH which in turn affects how phosphorus interacts with other cations, or by improving its retention through anion exchange. (Bashir *et al.,* 2018). Organic acids, through legend-induced dissolution, might remove phosphorus from mineral surfaces either competed with or displaced adsorbed phosphates for fixation sites on soil clay particles (Etesami & Jeong 2021). Cumulative phosphorus release after poultry litter biochar application and 20 leaching time was much lower for the more P retentive soil (Freitas *et al.,* 2020 & Gerges *et al.,* 2023). P-loaded biochars, particularly 600 ^{0}C, have the potential to keep soil available P at a noticeably higher level during the incubation period (Li *et al.,* 2020). Applying phosphorus fertilizers increased the amount of AB-DTPA extractable phosphorus in the soil considerably, especially when the rate of application was increased (Farid et al., 2023). Phosphorus release from the soils was described using various kinetic models (Habeeb *et al.,* 2023 & Beura *et al.,* 2021). According to our data, zero order and Parabolic diffusion equations show more R^2 than another fitted equation. In kinetics of P release performed (available P), it has been established that BC_2 releases phosphorus more quickly and in greater concentrations than other treatments (Fig 1). The results are consistent with those obtained by Morais *et al.,* (2023). They indicated that the kinetics of phosphorus release from fertilizers based on acidified biochar result in higher phosphorus concentrations in leachates. Gradual release is one of the characteristics of P biochar-based fertilizers, which contributes to increasing P availability (An et al., 2021). Habeeb *et al.,* (2023) confirmed that all used equations (first-order, diffusion and Elovich) have described the mechanism of P release from a solid phase to soil solution. According to Jia-qi *et al.,* (2023), all of the power function equation, parabola, Elovich, Michaelis and first-order predict the dynamics of P release that can be reached with coefficients of determination (R^2) greater than 0.964. First-order equations and Michaelis equations were preferred due to the value of (R^2) which reached 0.9922 and 0.9955. Models of mathematical and leaching were used to evaluate the efficiency and mechanism of P release. The second-order kinetic models and the Higuchi diffusion model were suitable to explain the P release mechanism (Phuon *et al.,* 2023).

4.3 Soil CO_2 flux and carbon mineralization kinetics

In this study, the BC_{400} and BC_{600} caused a decline in the cumulative CO_2 emissions compared to control treatment. Ali *et al.,* (2021) stated that, using biochar can lower gas fluxes by altering the microbial populations and soil qualities that may lower gas emissions. Also, Yang *et al.,* (2022) verified that the low in cumulative CO_2 fluxes values caused by biochar pyrolyzed at 450 and 600 ^{0}C could primarily be ascribed to the decreased soil organic matter availability after their addition. This was confirmed by a significant ($P < 0.05$) decrease in dissolved organic carbon content upon incubation at thirty days after adding biochar pyrolyzed at 450 and 600 °C. The amount and source of organic carbon have a significant impact on the soil CO_2 cumulative (Rahman 2013). Osman *et al.,* (2022) and Amin (2024) found that the cumulative CO_2 emissions increased significantly with increasing time of incubation in all treatments. Applying stable carbon into agricultural soils as biochar has been recognized as an effective tool for enhancing carbon sequestration into the soil to mitigate climate change (Roe *et al.,* 2021). The Parabolic diffusion kinetic and Zero-order models are commonly employed to depict carbon mineralization. The mineralization process is controlled by the initial soluble portion of organic carbon, as noted by Moreno-Cornejo *et al.,* (2014) whom determined a single rate of constant k. They indicated that the extensively retained carbon in the studied biochar is the least biodegradable elements, which helps to sequester carbon in the soil. Potentially mineralizable carbon (C_o) and C-mineralization rate were higher in grasslands than other land use types, indicating a higher rate of microbial activity and carbon cycling (Toh *et al.,* 2020). The size of microbial biomass carbon directly affects the model output (Zhang and Zhou 2018). Unlike the Zero-order model, most researchers have suggested that the first-order kinetic model describes the carbon mineralization process virtuously (Wu *et al.,* 2021 and Min *et al.,* 2023).

4.4 Fennel-Baladi parameters

These increases in Fennel vegetative growth may be due to that the biochar positively influenced growth, development of Fennel plant., It is so well preserved with nutrients and increased it, reduce loss of nutrient caused by erosion and/or leaching, improve water absorption, relieve soil density and enhance the growth of beneficial microorganisms. Bashir *et al.,* (2020) described that biochar application could accelerate plant development, growth and its yield due to several active substances in the biochar after pyrolysis process. The high P uptake could be attributed to the more solubilization effect of plant nutrients by the biochar addition that slowly released more nutrients insuring sustainable nutrients availability. These results are in agreement with those reported by Wang *et al.,* (2012) whom indicated that the biochar incorporation in ryegrass significantly improved P uptake. The increase microbial activity due to application of biochar could also be the other reason for the highest nutrient uptake in biochar treated soils (Nigussie *et al.,* 2012). When the kinetic equations are used, it becomes clear that the maximum amount of phosphorous released corresponds with the optimal times for the phosphorous plant's needs (Liu *et al.,* 2021), which gave the highest values for phosphorous release, especially (BC_2) treatment. For the role of dissolving complex phosphorous compounds in the soil, that causes releasing the most significant amount of available phosphorous for uptake by the plant (Liu *et al.,* 2019).

5. Conclusions

Acidified biochar-based fertilizers derived from fish waste have improved soil properties and considered a slow-release phosphorus (P) fertilizer. Chemical activation of biochar via H_2SO_4 was effective in promoting positive changes in biochar properties. Thus, contributed to a reduction in the soil acidity and reduces the CO_2 fluxes, at the same time, increased the P released. Relatively, compared to other treatments, the biochar has a high P release and potential mineralizable rate (Q) which was observed for BC_2 and BC_3 treatment. Phosphorus release and carbon mineralization kinetics from the acidified biochar using Zero-order and Parabolic diffusion were the best. Regardless the pyrolysis temperature, it's worth mentioning that acidified biochar at rate of 2% significantly increased the carbon footprints through maximum carbon mineralization compared to rate of 1%. Also, addition of biochar positively influenced vegetative growth, development of Fennel plants, the superior treatment that gives the highest increase in fresh, dry weight and NPK uptake by fennel plants was BC_2. It might be concluded that adding acidified biochar to the soil increases cumulative P release, improves fertility, quality of soil and plant growth.

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