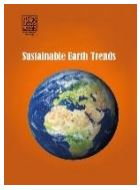
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Leonardite as a sustainable soil amendment to improve phosphorus release in calcareous soils: Implications for sustainable agriculture in arid regions

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ABSTRACT

In this study, a completely randomized design with 9 treatments at three replications was used to investigate the effect of Leonardite on the chemical behavior of phosphorus in a calcareous soil. The experimental treatments included a control group, three levels of phosphorus (100 and 200 mg/kg) supplied as monopotassium phosphate, Leonardite at four levels (0, 1, 3, and 5% w/w), and their combinations (P100L0, P100L1, P100L3, P100L5, P200L0, P200L1, P200L3, and P200L5). The phosphorus treatments were added to one kilogram of soil and maintained under controlled conditions for one month. Subsequently, the Leonardite treatments were applied to the soils, and incubation continued for 90 days. At the end of the incubation period, samples were taken from each treatment, and the amount of released phosphorus was measured at 2, 4, 8, 24, 48, 96, and 120 hours. The results of the kinetic investigations indicated that the addition of different levels of Leonardite increased the phosphorus (P) availability in the soil, which was attributed to the low pH and acidic functional groups present in Leonardite. The Elovich equation, with the highest coefficient of determination and the lowest standard error, was the best equation describing the kinetics of P release in the soil. This study confirmed that Leonardite application serves as an effective organic amendment in calcareous soils, significantly enhancing phosphorus availability while improving phosphorus uptake and utilization in plants. These findings demonstrated Leonardite's potential for advancing sustainable agriculture and supporting environmental conservation in arid and semi-arid regions.

ARTICLE INFO

Keywords:
Humic substances
Phosphorus availability
Phosphorus release kinetics
Soil incubation
Sustainable soil amendment

Article history:
Received: 01 November 2025
Accepted: 08 December 2025

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Citation:
Ayeene Heydari, M. et al., (2026). Leonardite as a sustainable soil amendment to improve phosphorus release in calcareous soils: Implications for sustainable agriculture in arid regions, *Sustainable Earth Trends:* 6(4), (136-145).

DOI: 10.48308/set.2025.242441.1164

1. Introduction

Phosphorus (P) is an essential macronutrient required by plants and other living organisms. Due to its critical physiological roles such as energy storage and transfer, preservation and transmission of genetic information, and maintenance of cell membrane integrity, P constitutes approximately 0.2% of plant dry weight (Almanassra et al., 2021). Despite plants ability to absorb P from the soil solution, many soils are inherently incapable of supplying adequate P for optimal growth, making the application of P fertilizers particularly in calcareous soils indispensable. Consequently, large quantities of phosphate fertilizers are applied annually. However, excessive and inefficient use of these fertilizers has led to P accumulation in soils, environmental contamination of water and soil resources, and adverse effects on the uptake of certain micronutrients (Gu et al., 2023). A significant portion of applied P becomes adsorbed onto soil solid phases, where it is retained as residual P (Glaser and Lehr, 2019). This accumulated P can gradually become available to plants in subsequent cropping cycles; in some soils, a single application of phosphate fertilizer may sustain crop requirements for several years without the need for reapplication (Glaser and Lehr, 2019). A large proportion of arable lands in Iran consists of calcareous soils, which

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typically contain more than 15% free calcium carbonate (Taalab et al., 2019). Crop production in these soils faces specific challenges, primarily attributed to high bicarbonate ion concentrations and elevated soil pH (Taalab et al., 2019). Because P and certain micronutrient availabilities are strongly pH-dependent, these elements are often immobilized and rendered unavailable to plants in such alkaline conditions (Li and Ahammed, 2023). Adsorption–desorption, precipitation–dissolution, and other P reactions in soil are key processes governing P availability in the soil solution (Singh et al., 2021). Soil components such as clays, carbonates, organic matter, iron and aluminum oxides, and their organo-metallic complexes significantly influence these reactions (Rosas-Ramírez et al., 2025). These processes ultimately determine P availability to plants, fertilizer requirements, and the environmental fate of P (Li et al., 2024). Soil organic matter is a critical component of the solid phase that profoundly affects P chemistry (Hartmann et al., 2023). Organic amendments can enhance P availability both indirectly by stimulating microbial activity and directly by lowering soil pH, complexing calcium ions, and solubilizing sparingly soluble P compounds (Nezami et al., 2018). Organic matter typically reduces P adsorption, maximum buffering capacity, and binding energy, thereby increasing P concentration in the soil solution (Oyetunji et al., 2022). Hu et al. (2024) reported that long-term application of organic materials promotes the retention of P in lower-energy binding forms, thereby enhancing its plant availability. Yang et al. (2019), in a study on black soils in northeastern China, observed that increasing organic matter content enhanced P adsorption in soils with pH > 6, but reduced it in soils with pH < 6. Leonardite is a naturally occurring oxidized lignite formed at shallow depths over geological timescales dating back approximately 650 million years (Yazdanpanahi et al., 2018) and is often referred to as natural biochar. Owing to its high humic acid content (30–80%), Leonardite is widely recognized as an effective soil conditioner (Ampong et al., 2022). Humic substances, including humic acids, modify the surface charge of soil particles, block adsorption sites, and consequently reduce P fixation (Etesami et al., 2021; Guo et al., 2023). Leonardite, due to its acidic, phenolic, and quinone groups, improves the availability of nutrients including phosphorus in calcareous soils which have low organic matter (Sharif Paghaleh et al., 2018). In their study on the effect of Leonardite on P adsorption behavior in a calcareous soil, Pashapour et al. (2024) reported that the use of Leonardite reduced P adsorption and increased P availability in soil resulting in reduction of the application of chemical fertilizers on a large scale.

In arid and semi-arid regions, agricultural productivity is chemically constrained by low phosphorus P availability, a consequence of high soil pH and calcareous properties. These conditions promote P fixation, leading to inefficient use and excessive application of P fertilizers. Organic amendments rich in humic substances like Leonardite, offer a potential solution by modifying soil P chemistry specifically through pH reduction and competition for adsorption sites to enhance P bioavailability. This study was designed to evaluate the combined effects of Leonardite and chemical P fertilizer on the kinetics and transformation of P in a representative calcareous soil from Kerman province, a region where such soils are widespread and face high P fertilizer inputs. By exploring strategies to improve P release efficiency and reduce dependency on synthetic inputs, this research supports sustainable land management goals. The integration of Leonardite represents a practical approach toward building more resilient and resource-efficient agricultural ecosystems in vulnerable drylands, ultimately contributing to sustainable soil fertility management and long-term agroecosystem conservation.

2. Material and methods

2.1. Measurement of physico-chemical properties of soil and Leonardite

A composite calcareous soil sample (Typic Argid) with low P content was prepared by combining five subsamples collected through random sampling from a depth of 0–30 cm in the Mahan area (coordinates: 30.26° N, 57.29° E), located in 15 km southeast of Kerman. After air-drying, the soil sample was passed through a 2-mm sieve and transferred to the laboratory for determination of selected soil physico-chemical properties. Particle size distribution and soil texture were determined using the pipette method (Gee and Bauder,

1986). Electrical conductivity (EC) and pH were measured in saturated paste and 1:5 soil-to-water extract for soil and a 1:20 Leonardite-to-water extract, respectively (Rowell, 1994). Organic carbon was determined by the wet oxidation method (Walkley and Black, 1934), selected for its established reliability in calcareous soils and cost-effectiveness. Calcium carbonate was measured by acid neutralization followed by titration with sodium hydroxide (Sparks et al., 2020). Available P in both soil and Leonardite was extracted according to the Olsen and Sommers (1982) procedure, and P concentration in the extracts was determined colorimetrically using the Murphy and Riley (1962) method.

Leonardite samples were collected from a coal mine in Kuhabnan County, Kerman Province, and after air-drying, the samples were thoroughly ground and passed through a 0.5-mm sieve. Functional groups of Leonardite were identified using an FT-IR spectrometer (Model TENSOR 27) in the wavenumber range of 400 to 4000 cm^{-1} (Barbeş et al., 2014). Elemental composition of the Leonardite, including carbon, hydrogen, nitrogen, and sulfur, was determined using a CHNS analyzer (Model ECS4010, Italy). The oxygen content in the leonardite samples was determined using Eq .1 (Palazzo et al., 2008).

$$\%O = 100 - (\%C + \%H + \%N + \%S) \quad (1)$$

2.2. Phosphorus release kinetics in soil

To investigate the effect of Leonardite on the chemical behavior of phosphorus, a completely randomized design with 9 treatments and 3 replications was conducted. The experimental treatments included: Control (Co), Two phosphorus levels (P100 and P200 mg/kg) supplied as monopotassium phosphate, Leonardite at four levels (L0, L1, L3, L5) corresponding to 0%, 1%, 3%, and 5% (w/w), and their combinations as P100L0, P100L1, P100L3, P100L5, P200L0, P200L1, P200L3, and P200L5. One kilogram of soil was weighed for each experimental unit and after application of phosphorus treatments (0, 100, and 200 mg P/kg), the samples were incubated under controlled temperature (25°C) and moisture conditions for one month. After this period, Leonardite was applied at four levels (0%, 1%, 3%, and 5% w/w), and the incubation continued for an additional 90 days. To study the P release kinetics, 1 g of soil from each treatment was weighed into centrifuge tubes containing 20 mL of 0.5 M sodium bicarbonate solution (pH 8.5). The samples were shaken for 2, 4, 8, 24, 48, 96, and 120 hours. At each time interval, the samples were centrifuged, and the P concentration in the solution was determined using spectrophotometry at 882 nm wavelength based on the molybdenum-blue colorimetric method. Various kinetic models were fitted to the experimental data including Elovich, Parabolic diffusion, pseudo-first-order, and pseudo-second-order equations (Table 1) (Wang et al., 2015). The coefficient of determination (R^2) and standard error (SE) parameters were calculated to evaluate the models' goodness-of-fit and to identify the best-fitting model.

Table 1. Kinetic equations used to fit phosphorus release data in treatments.

Equation number	Kinetic model	Equations	Coefficients
1	pseudo-first-order	$\ln q_t = \ln q_0 - k_1 t$	Absorption rate constant K_1 (s^{-1})
2	pseudo-second-order	$1/q_t = 1/q_0 - k_2 t$	[(mg P $kg^{-1})^{-1}$] Absorption rate constant K_2
3	Parabolic diffusion	$q_t = q_0 - k_p t^{1/2}$	[(mg P $kg^{-1})^{0.5}$] Absorption rate constant K_p
4	Elovich	$q_t = 1/\beta \ln(\alpha_s \beta_s) + (1/\beta_s) \ln t$	β_s [(mg P $kg^{-1})^{-1}$]; α_s (mg P kg^{-1} s^{-1}), The constants of the equation

q_0 :The amount of element released at T=0 q_t :Amount of element released at time t (seconds)

2.3. Statistical analyses

Statistical analyses were conducted using SPSS software (version 26) to evaluate the significance of treatment effects on soil phosphorus availability and related physicochemical parameters. One-way analysis of variance (ANOVA) followed by Duncan's multiple range test ($p < 0.05$) was employed to determine differences among treatments. For data visualization and modeling, nonlinear regression analyses and curve fitting were performed using GraphPad Prism (version 6) to describe the relationships between the studied parameters. Additionally, Microsoft Excel (2016) was used for preliminary data

organization, descriptive statistics to support the graphical interpretation of results.

3. Results and discussion

3.1. Selected physico-chemical properties of the studied soil and Leonardite

Selected physico-chemical properties of the studied soil and Leonardite are presented in Table 2. The studied soil exhibited a light texture, calcareous nature, and low organic matter content characteristics typical of soils in arid and semi-arid regions. In calcareous soils, high pH levels and low organic matter content lead to phosphorus fixation, rendering it less available for plant uptake (Shahabifar et al., 2018). With increasing geological age, the carbon content of Leonardite increases, while the contents of hydrogen, nitrogen, and oxygen decrease (Sharif Paghaleh et al., 2018). Previous studies have reported that Leonardite typically contains 51–68% carbon, 4.5–5.3% hydrogen, 1.0–1.4% nitrogen, 30–43% oxygen, and 0.2–0.5% sulfur (Sharif Paghaleh et al., 2018).

Table 2. Selected physico-chemical properties of the studied soil and Leonardite.

Soil Texture	Clay %	Loam %	Sand %	pH	EC dSm^{-1}	CCE %	OC %	Olsen-P $mgkg^{-1}$	C %	H %	N %	O %	S %
Sandy loam	12.5	36.8	50.7	8	0.8	37.5	0.4	7.9					
Leonardite	-	-	-	5.8			57	29.8	52.1	1.1	0.9	45.4	0.5

The FT-IR analysis confirmed the presence of diverse functional groups in the Leonardite sample that contribute to its reactivity in soil systems (Fig. 1), revealing characteristic absorption bands including a broad band at 3000-3400 cm^{-1} representing O-H and N-H stretching vibrations (Rani et al., 2024), a sharp peak at 1701 cm^{-1} indicating C=O stretching of carboxylic groups (Sarlaki et al., 2020), strong absorptions at 1610-1600 cm^{-1} corresponding to aromatic C=C and asymmetric -COO stretching (Khosravi et al., 2023), bands at 1000-1200 cm^{-1} demonstrating aromatic C-O-C ether linkages and polysaccharide C-O vibrations (Rani et al., 2024), peaks at 797-777 cm^{-1} confirming substituted aromatic structures (Sarlaki et al., 2020), and minor bands at 535-474 cm^{-1} revealing silicate impurities through Si-O stretching (Sarlaki et al., 2020). The abundance of acidic functional groups, particularly carboxylic and phenolic groups, provides multiple binding sites for nutrient complexation (Khosravi et al., 2023), enhancing phosphorus availability through ion exchange processes, chelation of metal ions that would otherwise immobilize phosphorus, and creation of negative charges that improve nutrient solubility (Nargesi et al., 2022). The presence of both hydrophilic (hydroxyl, carboxylic) and hydrophobic (aromatic) domains further supports Leonardite's capacity to interact with diverse soil components and nutrients, making it particularly effective in calcareous soils where phosphorus availability is typically limited (Sharif Paghaleh et al., 2018).

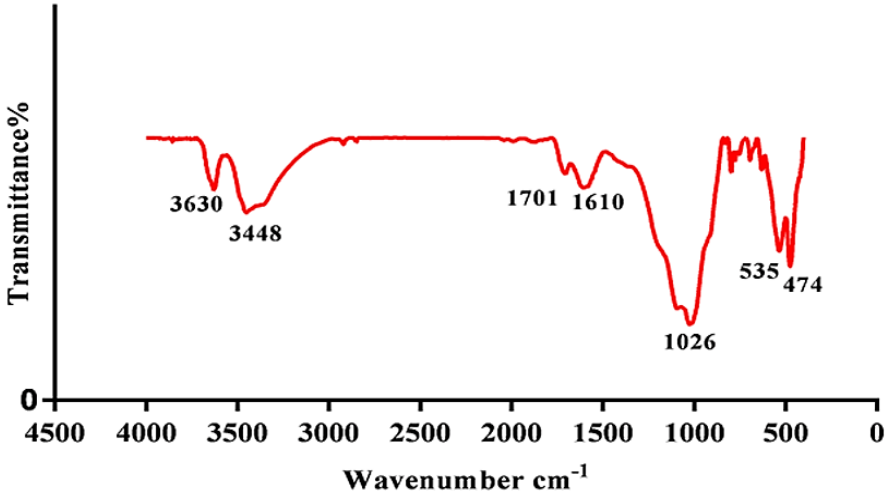


Fig. 1. FT-IR spectroscopy of the studied Leonardite.

3.2. Phosphorus release kinetics

Fig. 2 illustrates the cumulative phosphorus release from control soil, and other treatments. As can be seen, the phosphorus release is consistently higher in all Leonardite treatments compared to the chemical fertilizer treatment, while the lowest release is occurred in the control. The P release pattern in organic treatments is different from that in chemical treatments, so that in all Leonardite-amended soils, phosphorus release increased progressively with time and reached its maximum at 120 hours which can be attributed to the acidic nature of Leonardite and the abundance of oxygen-containing functional groups. As shown in Fig. 3, the FT-IR spectra of the studied treatments revealed distinct differences. In Leonardite-treated samples, multiple peaks appeared in the 2500-3600 cm^{-1} range which can be attributed to the phenolic hydroxyl (-OH) groups. This observation was further supported by the presence of an aromatic ring bending vibration peak near 1100-1200 cm^{-1}. These peaks were either absent or significantly weaker in the chemical fertilizer P and Co samples. Additionally, a peak at approximately 1799 cm^{-1} was observed, which may correspond to aromatic C=C stretching, carbonyl (C=O) stretching from ketones or quinones, or amide-related C=O groups. The peak in the 1100-1200 cm^{-1} range assigned to aromatic ring bending or aliphatic C–H bending also exhibited greater intensity in Leonardite-treated samples. Comparative spectral analysis confirmed that the phenolic –OH peak was obviously more intense in Leonardite-amended soils, indicating a higher abundance of phenolic functional groups. These results demonstrate that Leonardite introduces acidic functional groups into the soil matrix, and decreases soil pH which is in consistent with findings by Bolan et al. (2024), who reported increased extractable phosphorus in alkaline soils amended with biochar rich in acidic functional groups. Acidic functional groups on Leonardite surfaces modify the surface charge of soil particles and due to some steric effects, which have an extensive spatial structure, cause to block the surface adsorption sites and reduction of P fixation. (Guo et al., 2023). Additionally, Zhu (2018) reported that biochar can enhance phosphorus availability through anion or cation exchange mechanisms involving functional groups that interact directly with phosphate ions. In contrast, in both chemical fertilizer treatments (P100 and P200), the highest phosphorus release occurred within the first 48 hours, followed by a relatively stable trend, which can be attributed to the rapid adsorption of phosphate onto soil constituents. Based on coefficient of determination (R^2) and standard error values (Table 3), Pseudo-first-order, Parabolic diffusion, and Elovich equations effectively described phosphorus release from Leonardite-treated soils, whereas Pseudo-second-order model showed a poor fit due to low R^2 values. Among all models, the Elovich equation provided the best fit, exhibiting the highest R^2 and lowest standard error. This aligns with Zhao et al. (2021), who identified the Elovich model as the most suitable for describing phosphorus release in calcareous soils amended with organic fertilizers.

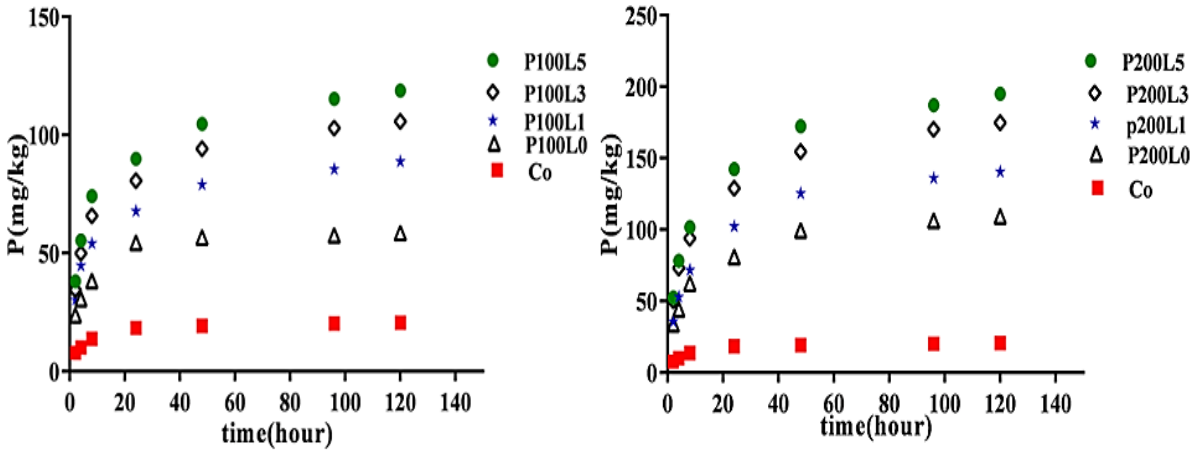


Fig. 2. Cumulative phosphorus released from soils treated with different levels of Leonardite and chemical fertilizer: C control, P: 3 levels of phosphorus including 0, 100, 200 $mgkg^{-1}$ from potassium monophosphate source and L0, L1, L3 and L5: Leonardite at 4 levels of 0, 1, 3 and 5 wt%, respectively.

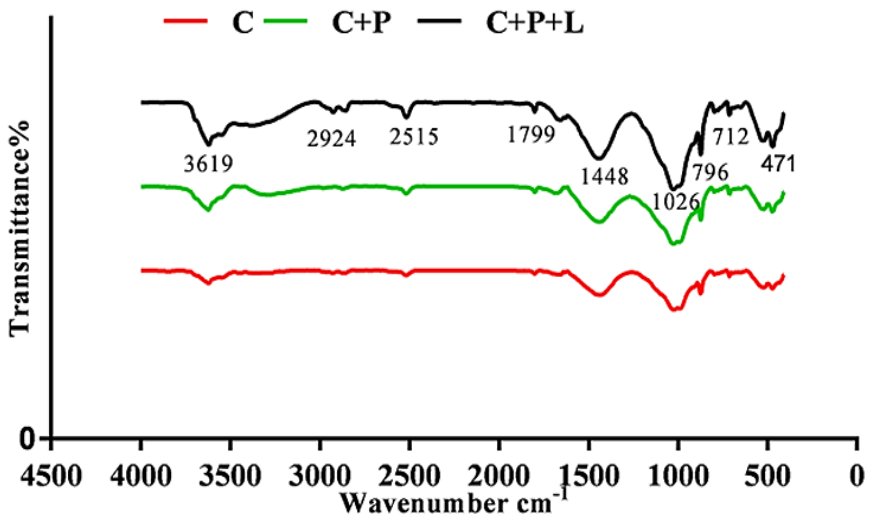


Fig. 3. FT-IR spectroscopy of samples treated with Leonardite and chemical fertilizer (C+P+L), chemical fertilizer (C+P) and control sample (C) after 90 days of incubation

Table 3. Parameters of kinetic equations used for phosphorus (P) in fitting the released phosphorus data (P) in the treatments of Leonardite (L), chemical fertilizer and control sample (Co).

Treatment	Pseudo-first-order			Pseudo-second-order			Parabolic diffusion				Elovich			
	SE	r^2	k_1	SE	r^2	k_2	SE	r^2	Kp	q_0	SE	r^2	A	B
CO	1.25	0.95	0.1818	1.16	0.95	21.12	2.43	0.81	1.231	8.951	0.49	0.99	23.81	0.3136
P100L0	3.92	0.94	-0.7870	3.89	0.93	-60.48	7.36	0.78	-3.381	26.98	2.07	0.98	58.82	-0.0044
P100L1	8.13	0.88	0.1770	3.51	0.89	62.25	7.35	0.90	5.515	33.76	2.09	0.99	77.12	0.0723
P100L3	9.15	0.90	0.1661	7.15	0.88	61.25	9.62	0.89	6.796	38.58	2.78	0.99	78.73	0.0585
P100L5	10.34	0.90	0.1657	7.75	0.89	85.22	10.77	0.89	7.657	42.76	3.25	0.99	85.84	0.0520
P200L0	9.81	0.91	-0.1301	8.01	0.88	-82.21	10.13	0.90	-7.641	34.28	3.05	0.99	56.18	-0.0524
P200L1	11.44	0.93	0.1034	7.75	0.89	75.21	13.40	0.91	10.56	36.44	3.17	0.99	51.57	0.0380
P200L3	15.87	0.91	0.1235	9.01	0.88	81.23	15.92	0.92	12.43	51.93	2.70	0.98	81.72	0.0333
P200B5	16.97	0.92	0.1145	10.40	0.88	77.25	17.49	0.91	14.14	54.40	3.56	0.99	85.28	0.0284

Fig. 4 visually represents the fitted phosphorus release curves for Leonardite, chemical fertilizer, and control treatments. Given that calcareous soils in arid and semi-arid regions are typically characterized by low organic matter content and high pH key factors limiting phosphorus availability the presence of acidic functional groups like carboxylic and phenolic in Leonardite-amended soils appears to be the primary mechanism driving phosphorus desorption from soil surfaces. This mechanism, mediated by gradual pH reduction and surface site blocking over time, is consistent with the findings of Bolan et al. (2024).

3.3. Phosphorus transformation rate

To determine the phosphorus transformation rate in the studied soil in comparison with treatments, kinetic rate coefficients were extracted from the kinetic equations (Table 3). The slope of these kinetic equations can be used as an indicator of the phosphorus transformation rate in soil (Matin et al., 2020). The results showed that the rate constants differed between Leonardite-amended, chemically fertilized, and control samples. Specifically, the rate constants for the chemical fertilizer treatments were negative, indicating that during the incubation period, phosphorus was progressively converted into more stable, less available forms in the soil. In contrast, the positive values of the rate constants in Leonardite-amended samples suggest two concurrent processes: (1) the addition of soluble phosphorus from Leonardite, and (2) the transformation of native stable phosphorus fractions into more plant-available forms (Reza et al., 2024). This implies that Leonardite not only contributes phosphorus directly but also enhances the mobilization of existing soil phosphorus pools. Interestingly, increasing Leonardite application levels (from 1% to 5%) did not significantly alter the kinetic rate constants. This suggests that beyond a certain threshold, higher Leonardite doses not further accelerate phosphorus transformation kinetics in soil, and is not cost-effective. Furthermore, analysis of the Elovich equation parameters, which describes kinetics on heterogeneous

surfaces, revealed that in Leonardite-treated samples the coefficient β (desorption constant representing the activation energy for diffusion) decreased, while the coefficient α (initial desorption rate constant) increased compared to the control. This indicates that Leonardite treatment simultaneously enhanced the initial release of phosphorus and reduced the energy barrier for subsequent phosphorus desorption. This pattern confirms a greater amount of phosphorus was released in Leonardite-amended soils. As noted by Timofeeva et al. (2022), the Elovich parameters α and β are widely used to compare the release dynamics of anions such as phosphate across different soils. They further emphasized that an increase in α coupled with a decrease in β reflects enhanced phosphorus release and availability in soil observations fully consistent with the findings of the present study.

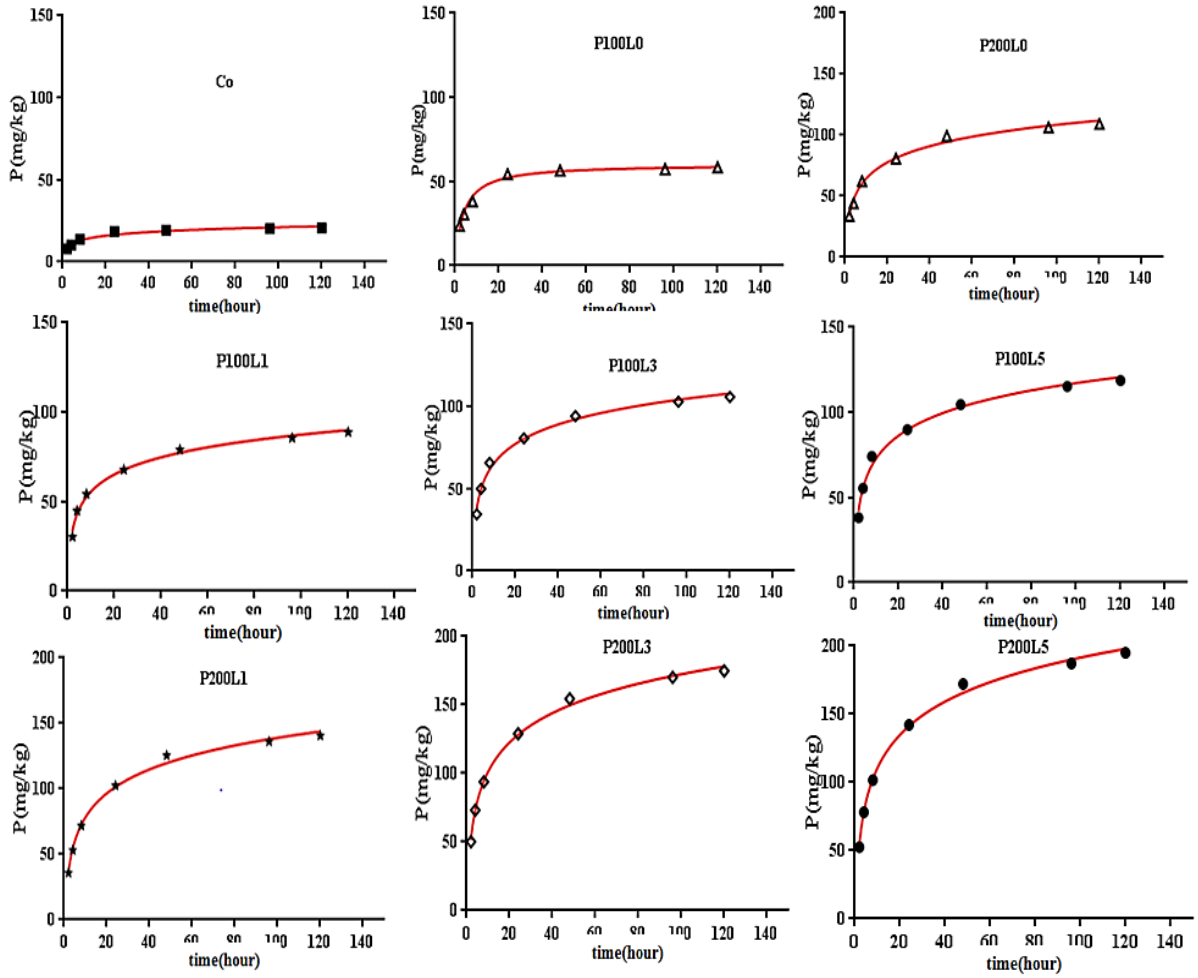


Fig. 4. Fitting the Elovich equation to the released phosphorus (P) data in the treatments of Leonardite (L), chemical fertilizer and control sample (Co).

4. Conclusion

This study demonstrated that Leonardite, as natural organic amendment rich in humic substances and acidic functional groups, significantly enhanced phosphorus availability in a calcareous soil through reducing P fixation, decreasing soil pH, and promoting the transformation of stable P forms into plant available pools. The Elovich kinetic model best described the P release kinetics, and the positive rate constants in Leonardite-amended soils confirmed the active mobilization of phosphorus over time contrasting with the negative transformation rates observed in chemically fertilized soils, where P tended to become immobilized. These findings highlighted the potential of Leonardite to improve the efficiency of phosphorus fertilizers in arid and semi-arid regions, where calcareous, low organic matter soils dominate and P deficiency is a major constraint to agricultural productivity. By reducing reliance on high rates of synthetic P fertilizers whose overuse contributes to resource depletion, environmental pollution, and economic burden

Leonardite offers a practical, low-cost, and eco-friendly strategy for sustainable soil fertility management through the conservation and sustainable use of terrestrial ecosystems. While the short-term incubation results are promising, scaling this strategy requires long-term field validation under real farming conditions. Nonetheless, integrating natural amendments like Leonardite into nutrient management systems represents a meaningful step toward resilient, resource-efficient, and environmentally sound agriculture in vulnerable dryland regions contributing not only to food security but also to the broader vision of sustainable development. However, the results showed that the application of leonardite at 5% level did not significantly increase the available P level compared to the 3% level. Accordingly, the 3% leonardite level was recommended as the optimal level of leonardite for soil application in calcareous soils.

Acknowledgements

This study was partially based on the Ph.D. dissertation of the first author. The authors gratefully acknowledge the support and facilities provided by the Department of Soil Science, College of Agriculture, Shahid Bahonar University of Kerman, Kerman, Iran. The authors also extend their sincere appreciation to Mr. Majidi Kohbanani for her technical assistance in the preparation of the Leonardite sample.

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