

# The Comparative Study on the Influence of Inorganic Soil Amendment on the Growth and Leaching Analysis of the *Brassica* Family

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#### **1. Introduction**

Agriculture plays a crucial role in the socioeconomic progress of a nation since it is a key component and determinant of national development. The agricultural sector in Malaysia has

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experienced significant progress and advancement due to the successful implementation of modern technology, resulting in increased crop yields. The agriculture sector in Malaysia constitutes almost 20% of the country's gross domestic product (GDP), establishing it as a prominent industry within the nation [1]. Malaysia's economy has undergone substantial changes and advanced through three primary phases over the last fifty years: agrarian (1960 - 1974), industrial (1975 - 1999), and urbanization (2000 - present) [2]. The government designated the agriculture industry as important under the Movement Control Order (MCO), allowing firms to continue their operations. Currently, Malaysia is facing new challenges in the pursuit of innovative findings that might contribute to the progress of its agriculture and food industry. The primary group of vegetables in Malaysia consisted of the Brassicaceae family, which included broccoli, Brussels sprouts, cauliflower, kale, mustard (greens), and collards. Essential minerals, including calcium (Ca), iron (Fe), and potassium (K), as well as vitamins such as riboflavin and thiamine, are found in significant quantities in mustard greens. Additionally, these substances contain advantageous constituents such as zinc, selenium, phosphorus, and folate, which are recognized for their utilitarian dietary characteristics [3].

The fertilizer, which acts as a nutrient and enhances soil conditions, plays a pivotal role in the growth of plants. The utilization of fertilizer inputs enhances crop productivity; however, ineffective administration and over-application of fertilizers can result in a decline in fertilizer utilization efficiency, as well as the build-up and depletion of nutrients in the soil. Leaching refers to the process of ions being released in a soluble condition as water passes through the soil profile, leading to their removal [4]. The leaching of nutrients, namely nitrogen and phosphorus, poses a significant environmental risk and can potentially harm human health. Therefore, it is crucial to use effective and cautious management measures. Nitrogen is the predominant element in the Earth's atmosphere and can be found in various forms, including elemental nitrogen, nitrate, and ammonia. Nitratecontaining fertilizers may exhibit a greater rate of nitrate discharge compared to fertilizers based on ammonium. Nitrogen is the predominant element in the Earth's atmosphere and can be found in several forms, such as elemental nitrogen, nitrate, and ammonia. Every natural and human-caused source of nitrogen possesses the capability to contribute to the contamination of groundwater with nitrates [5]. The generation of nitrate and ammonium ions arises from the inherent interactions between atmospheric nitrogen and precipitation. The leaching of nitrates from fertilizers is influenced by the specific type of fertilizer employed (ammoniacal, nitrate, or organic), the method of application, and the prevailing environmental conditions.

Soil enhancements such as zeolite, offer notable advantages in terms of nutrient retention and address the issue of soil leaching. Due to its high solubility and lack of soil retention, nitrate easily infiltrates groundwater and causes contamination [6]. This results in an elevation of nitrates beyond the acceptable threshold, which might give rise to health complications. A soil amendment refers to any chemical that is introduced into soil to enhance its physical characteristics, including but not limited to water retention, permeability, water infiltration, drainage, aeration, and structure [7]. According to reports, the incorporation of organic and inorganic soil amendments can elevate the soil's pH by a range of 3.2 to 7, reduce the solubility of trace metals by over 80%, and enhance soil stability [8,9].

Kaolinite, a hydrated aluminosilicate mineral, is the main constituent of the commercially available clay known as kaolin. The determination of kaolin's commercial worth is contingent upon its whiteness and its ability to maintain a thin, manageable particle size [10]. The use of kaolin has been found to significantly enhance plant height, encompassing root length, leaf size, and biomass. However, it does not appear to have any impact on the chlorophyll content of leaves [11]. In the context of sub-optimal watering conditions, it was observed that a kaolin concentration of 3% had the most significant influence on grain growth [12]. Therefore, the specific surface area (SSA) is

elevated, leading to a substantial ability to retain cations and anions. This is highly advantageous for agriculture as it safeguards the cationic and anionic forms of plant nutritional components from leaching during heavy rains in the wet tropics [13]. In natural environments, kaolin commonly has diverse proportions of other minerals such as muscovite, quartz, feldspar, and anatase [14]. Kaolin is frequently used in agriculture for insect control. However, the agricultural use of kaolin exceeds that amount. Not only does it defend the plant from external threats, but it also enhances the quality of the produce. Due to its hydrophilic quality, minimal heat conductivity, and pH range between 4 and 9, kaolin clay is simple to disperse in water [15]. Deposits of kaolin are utilized in numerous industries, including the production of paper, plastic, rubber, pigments, paints, adhesives, zeolite, pharmaceuticals, and nanocomposite materials. Kaolin is one of the sophisticated materials with a wide range of applications [16].

The calcined anhydrous form of the clay mineral kaolinite is called metakaolin. By heating kaolin to a specific temperature range, a hydroxyl group is removed from the kaolin, resulting in a chemical transformation. During calcination, the orientation of octahedral strata changes to tetrahedral [17]. Temperature and time vacillate during the calcination phase, and the arrangement layer becomes extremely unstable. In most instances, a temperature between 550 and 600 <sup>o</sup>C is chosen; the phase does not become more stable until 900  $^{\circ}$ C, whereas 1050  $^{\circ}$ C is required for the formation of mullite [18]. During calcination at temperatures between 650 and 700  $^{\circ}$ C, structural hydroxyl groups are eradicated, resulting in a bulky product with improved resilience and opacity, both of which are desirable qualities for paper coating applications. Alternately, by thermally heating kaolin at 1000- 1050  $^{\circ}$ C, a 92-95% increase in luminosity can be achieved, despite the material's increased abrasiveness [19]. Metakaolinization at temperatures greater than 700 °C is more suitable for the synthesis of zeolite NaX [20].

The predominant sources of natural zeolites are hydrothermal and volcanic. Clinoptilolite, mordenite, and chabazite are zeolites that are naturally found in nature and hold practical significance [21]. Some of the most often utilised zeolites include clinoptilolite, heulandite, natrolite, Phillip site, laumontite, mordenite, chabazite, stilbite, harmotome, ferrierite, analcime, and erionite [22]. Volcanic (basalt-andesite-rhyolite) and volcanic-sedimentary rocks undergo hydrothermal, hydrothermal-metasomatic, diagenetic, and metamorphic processes at temperatures of 250 °C and pressures ranging from 200 to 300 MPa [23]. Commercial utilization of both natural and synthesized zeolites is attributed to their distinctive adsorption, ion exchange, molecular sieve, and catalytic characteristics [23]. The principal applications of synthesized zeolites include catalysts, surfactants, and molecular filters [24]. Zeolites are widely recognized for their ability to resist ion exchange and reversible dehydration [25]. The three-dimensional tetrahedral framework is a fundamental structural feature of zeolites, wherein each oxygen atom is shared by two tetrahedra [25]. The synthesis of hydrothermal zeolite is a complex process that involves the crystallization of many phases, usually including a liquid phase and both amorphous and crystalline solid phases [26]. The process of hydrothermal synthesis involves the production of a singular crystal, which is facilitated by the solubility of minerals in hot water under conditions of elevated pressure. The utilization of zeolite in agriculture, namely for crops, offers benefits due to its ability to assimilate nutrients from the sediment and disperse them evenly throughout all plant components. Zeolite stimulates the growth of plants by mitigating nitrogen depletion in the soil [27].

Zeolites are classified as crystalline aluminosilicates and exert a significant influence on soil enhancements through their ability to facilitate soil aeration, enhance nutrient availability, and augment plant productivity [28]. The International Zeolite Association has formally acknowledged and verified 230 more zeolites and zeotype frameworks, in addition to the 60 zeolites that occur naturally [29]. Zeolites are a commonly employed substance that can be employed as a cost-effective solution to alleviate the adverse impacts of heavy metal toxicity [28]. Zeolites exhibit a porous threedimensional structure that facilitates water retention and improves nutrient availability for plants [30]. Furthermore, it should be noted that zeolites exhibit a significant cation exchange capacity (CEC) [31,32]. The utilization of natural zeolite is advised for eliminating or stabilizing heavy metals, including Cd, Zn, Pb, and Ni, from soil that has been contaminated as a result of human activities. This recommendation is based on the zeolite's notable ion-exchange capacity and porous structure [33]. Multiple studies have shown that zeolite exhibits favorable outcomes in terms of mitigating nitrate leaching and promoting crop growth, which can be attributed to its porous properties [34]. According to reports, the incorporation of zeolite has been found to improve the accessibility of nutrients and water for plant roots through the facilitation of soil aggregation and the augmentation of soil cation exchange capacity (CEC) [35].

All zeolites function as filters for particles, selectively absorbing them based on their size [36]. Zeolite has been employed not only for water and wastewater purification but also for the elimination of ammonia and heavy metals [37,38]. The high-water retention capacity of zeolite has been found to promote soil electrical conductivity, water absorption, and nutrient conservation [39]. The utilization of this methodology resulted in an increase in physical properties, namely in terms of permeability and moisture content. Moreover, it effectively reduces soil erosion by reducing the amount and speed of flow during periods of drought or water stress, when the soil experiences increased humidity, nutrient depletion, and vulnerability to erosion [40,41]. Zeolite exhibits a substantial surface area that exhibits an affinity for microbes. The high porosity, cation exchange capability, and specific affinity for ammonium and potassium cations of this feature make it advantageous in the agricultural sector [42]. Moreover, zeolite can serve as a medium for mineral transportation [43].

The expanded structure of perlite renders it highly porous, enabling it to absorb water and improve drainage. Consequently, it serves as a superb supplement to compost, facilitating efficient water dissipation. Perlite is advantageous for both seed germination and vegetative propagation of plants. Vermiculite, grit, and sharp sand also have similar functions [44]. Furthermore, perlite is employed for purifying water, chemicals, and pharmaceuticals. Perlite can be employed to enhance the drainage and aeration of soilless mixtures and to augment the oxygenation of plant roots. It serves as an independent component in hydroponic horticulture systems to facilitate the sprouting of seeds, the establishment of root cuttings, and the stabilization of root systems. Perlite has the potential to be employed either in combination with other chemicals or as a standalone treatment during the growth of flowers, vegetables, and fruits. Before incorporating offshoots, it is imperative to hydrate the perlite when employing it solely for the objectives of folding and filling. The capacity of perlite to retain moisture is only ascribed to this feature. Perlite provides an ideal medium for the growth of roots. Nevertheless, by avoiding the use of costly vegetable seeds, one can achieve higher earnings. Perlite reduced the accessibility of potassium (K), phosphorus (P), and arsenic (As) in the root-soil system [45]. This study intended to focus on analyzing the effectiveness of soil amendment (kaolin, metakaolin, zeolite, and perlite) towards plant growth (physical analysis) and reducing the leaching of concentration nitrate and nitrite in the Brassica family (mustard green and kale).

# **2. Methodology**

# *2.1 Kaolin, Metakaolin, Zeolite and Perlite*

The kaolin utilized in the current investigation was provided by Deltacorp Sdn. Bhd, a Malaysian company. The metakaolin approach involved placing 50g of kaolin in the crucible and subjecting it to a four-hour heating process at 600 <sup>o</sup>C in the furnace. A 1M NaOH solution was carefully combined

with 60 milliliters while using roughly 3 grams of metakaolin combination and underwent continuous agitation at a temperature of 40  $^{\circ}$ C for 24 hours during the aging phase. To mitigate the occurrence of evaporation and desiccation, the mixture was subjected to blending inside a controlled environment. Following the completion of the aging procedure, the solution was consistently transferred into a 100 mL autoclave lined with Teflon to facilitate the crystallization step. The crystallization procedure was carried out at a concentration of 100 °C for nine hours. Subsequently, the mixture will be expeditiously cooled on a tray that is loaded with cold water. The liquid component was collected and subjected to multiple rinsing cycles until the pH of the solution decreased to a value below 9. The solid residue underwent a heat treatment for 12 hours in an oven maintained at a temperature of 60 °C. The perlite was obtained directly from Multifilla (M) Sdn. Bhd is located in Selangor, Malaysia. The particle size range of the material is from 0.15mm to 2.5mm. The kaolin, metakaolin, zeolite, and perlite were characterized to determine their chemical composition through X-ray fluorescence Spectrometer (XRF) and X-ray diffractometer (XRD) while structure characterization methods using the scanning electron microscope (SEM).

# *2.2 Experiment Procedure*

The pot experiment was conducted in a greenhouse at Politeknik Jeli Kelantan in 2023. The average diurnal and nocturnal temperatures for the experiment were 36  $^{\circ}$ C and 25  $^{\circ}$ C, respectively. Each container was filled with 700g of organic soil and supplemented with NPK Green 15:15:15 fertilizer for plant cultivation. The composition of green NPK fertilizer includes the chemical components nitrogen (N), phosphorus (P), and potassium (K). There was a total of 7 primary treatments undertaken for this trial, as indicated in Table 1. The plant was being irrigated twice daily, once in the morning and once in the evening.



# *2.3 Data Analysis*

A linear analysis of variance (ANOVA) was conducted to ascertain the efficacy of soil amendment on plant development. Following the least significant difference (LSD) test with a significance level of p < 0.05, lowercase letters in the figures indicate statistically significant differences. The treatments were compared using the Least Significant Difference (LSD) test at a significance level of 0.05, as described [46]. The figures were generated using Excel 2020, and the data was examined using SPSS version 10.

# **3. Results**

## *3.1 Material Analysis*

Table 2 displays the utilization of XRF for the assessment of the chemical composition of kaolin, metakaolin, zeolite, and perlite. Kaolin, which consists of 48.72% SiO<sub>2</sub> and 37.63% Al<sub>2</sub>O<sub>3</sub>, was utilized as a Si and Al source in the manufacturing process of zeolite. The synthesis of several Zeolite LTA compounds was achieved using a combination of kaolin, silica, and alumina without any modifications based on XRF analysis. The SiO<sub>2</sub> content in metakaolin increases from 48.72% (in kaolin) to 50.73%, while the  $Al_2O_3$  content falls from 37.63% (in kaolin) to 36.34%. In the case of zeolite, the percentages of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and NaO are 46.75%, 40.12%, and 13.13%, respectively. Perlite is composed of many chemical constituents, including  $SiO_2$  at a concentration of 72.2%, Al<sub>2</sub>O<sub>3</sub> at 12.9%, Fe<sub>2</sub>O<sub>3</sub> at 0.5%, CaO at 0.2%, Na<sub>2</sub>O at 2.3%, and K<sub>2</sub>O at 3.45%.

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The chemical composition of kaolin, metakaolin, zeolite, and perlite



The X-ray diffraction (XRD) pattern of the raw kaolin and kaolinite at 2θ angles of 12.398° and 24.944°, respectively, is depicted in Figure 1 [47]. The results of the analysis suggest that the sole mineral detected is kaolinite, which constitutes the entirety of the composition. After calcination, the X-ray diffraction (XRD) pattern of metakaolin experiences modifications, which are marked by shifts and variations in the peaks' strengths. At a temperature of 600  $^{\circ}$ C, the observed changes fall within the range of 2θ= 20.861 and 26.644. Moreover, a significant increase in amorphization was seen, as the strength of the kaolinite peaks decreased and the occurrence of amorphous  $SiO<sub>2</sub>$  phases became more apparent. The latest conclusion is consistent with the results reported by Adebanjo *et al.,* [48], indicating that alterations in the characteristics, makeup, and geological origin of kaolin minerals may serve as a credible rationale. The manufacture of zeolite is distinguished by the existence of 10 unique peaks located at certain places on the 2θ scale. The peaks described in Figure 1 are situated at 2θ values of 10.158, 12.449, 16.093, 20.397, 20.857, 21.649, 23.966, 26.089, 26.637, 27.092, 29.916, 30.804, 32.515, and 34.150 [47]. The peaks observed in the X-ray diffraction (XRD) pattern exhibit a strong resemblance to the XRD patterns observed in single-phase zeolite-LTA and zeolite A. When subjected to a 1M NaOH solution, the Zeolite-LTA has the greatest degree of crystallinity, reaching 86.80%.

*Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* Volume 124, Issue 1 (2024) 79-92



**Fig. 1.** XRD analysis of (a) kaolin, (b) metakaolin, (c) zeolite

The hexagonal plate structure of kaolinite crystals through the utilization of scanning electron micrographs (Figure 2) [47]. The morphologies of untreated kaolin have a lamellar structure [49]. Moreover, the photograph exhibits minuscule particles that are perceptible. Moreover, Figure 2 illustrates that the kaolin clay in its unprocessed form displays a crystalline morphology characterized by layered structures. This finding aligns with a prior study that examined the mineralogical diversity observed in kaolin from Malaysia [50]. After doing a more in-depth examination of the micrograph, it was ascertained that every specimen had irregular platelets and a granule with a sub-rounded morphology. The calcination process yielded metakaolin with a high degree of disorder, an amorphous structure, and a sheet-like shape [47]. The scanning electron microscope image presented in Figure 2 confirms the exact alignment of the manufactured Zeolite-LTA with the cubic crystalline system family. The presence of well-crystalline zeolite crystals with a cubic morphology and consistent diameters was observed. The chemicals synthesized after 6 and 20 hours had unique cubic crystal forms, as evidenced by the scanning electron microscopy photographs [51].







**Fig. 2.** SEM image of (a) kaolin, (b) metakaolin, (c) zeolite, (d) perlite

# *3.2 Plant Growth Analysis*

Based on the statistical analysis conducted at harvest 1 (Table 3), a one-way ANOVA was performed to compare the means. According to Table 3, at harvest 1, zeolite amended in soil shows a higher significance difference in mustard green height, width of leaves, and weight of shoot and root compared to other treatments, while in kale, zeolite shows a higher significance difference only in weight of dry shoot and leaves. Zeolite shows no significant difference in the number of leaves for both brassica families. Zeolite also shows a significant difference in the diameter stem of mustard green compared to standard and low NPK. In addition, zeolite indicates a higher significance difference in kale height compared to standard and low NPK while there is no significant difference in the width of leaves and diameter of stem compared to other treatments. Kaolin, metakaolin, and perlite show slightly higher significance differences for all the plant growth characteristics compared to standard and low NPK.

#### **Table 3**

Plant growth characteristics for mustard green and kale at harvest 1. Mean has been given different letters in the same column; they are significantly different at p≤0.05



According to Table 4, at harvest 2, zeolite show a higher significance difference for the diameter stem of mustard green compared to other treatments. Unfortunately, zeolite shows no significant difference in the number of leaves of mustard green compared to other treatments but, the height of mustard green shows a higher significance difference in zeolite amended compared to standard and low NPK. Zeolite also shows a significant difference in leaves mustard green compared to other treatments except for metakaolin. For kale height, zeolite and perlite show a higher significant difference compared to standard and low NPK. At harvest 2 also, for kale, zeolite amended showed a higher significant difference in diameter of the stem, number of leaves, the weight of shoot and leaves, and weight of dry shoot and leaves compared to other treatments. The same observation applies to the barley crop, where a 5% Zeolite treatment resulted in taller plants, as well as more grains and plant biomass compared to a 1% Zeolite treatment [52]. The observed response could perhaps be attributed to the interplay between water, salt, and nutrients within soils that have been combined with zeolite. Furthermore, the observed increase in growth can be ascribed to the essential nutrients included in zeolite. The use of zeolite has led to improved cation exchange capacity, increased water retention, and greater nutritional availability for plants [53,54].

In addition, the use of zeolite resulted in significantly improved growth characteristics of broccoli cultivated throughout the dry season as compared to the control group. The attributes encompass plant width, stem diameter, duration until 50% flowering, and duration until 50% harvest [55]. The application of zeolite at a rate of 4 to 8 tonnes per hectare resulted in a significant increase in the yields of wheat, aubergine, and apple, with respective increases of 13-15%, 19-55%, and 13-38% [56]. The stimulation of plant development can be attributed to the heightened concentration of essential nutrients, including nitrogen, phosphorus, potassium, calcium, magnesium, and micronutrients [57]. The zeolite effectively keeps nutrients inside the root zone, enabling plants to utilize them as needed [58]. The utilization of zeolite has been found to have a beneficial impact on the growth and production of plants. The observed results can be attributed to a significant improvement in the efficiency of soil nitrogen, ranging from 10% to 22%. Furthermore, empirical evidence has demonstrated that the utilization of zeolite yields substantial decreases in nitrogen leaching, ranging from 86% to 99% [59,60].

Further, zeolites provide numerous advantages in agriculture, including their ability to retain a substantial quantity of water. The significance of this factor is paramount during periods of water shortage, particularly in areas characterized by limited water resources or substantial water depletion [61]. The application of a greater quantity of zeolite to the soil is linked to a decline in crop growth as a result of diminished drainage capacity and a shift in water availability towards elevated levels of soil humidity. Additionally, the application of zeolite on strawberries and blackberries led to increased agricultural productivity and enhanced fruit characteristics, specifically about soluble solids and total acid concentrations [62]. The authors noted that zeolites possess distinct attributes that contribute to improved efficiency in fertilizer and water utilization, stimulation of crop growth, augmentation of yield and fruit quality, and a favorable influence on mitigating environmental pollution through the reduction of nitrate leaching and emissions of nitrous oxides and ammonia [62].

#### **Table 4**

Plant growth characteristics for mustard green and kale at harvest 2. Mean has been given different letters in the same column; they are significantly different at p≤0.05



## *3.3 Leaching Analysis*

Based on Table 5, soil amended with zeolite shows the lowest nitrite concentration every week for both plants. For nitrate concentration, zeolite did not show a lower value compared to other treatments in mustard green but a lower concentration in kale. Applying ground zeolite to apple trees before planting, at rates of 30, 45, and 60 t/ha, resulted in a significant rise in soil nitrogen and potassium levels by 2 to 3 times [63]. Additionally, it enhanced the sugar content, and vitamin C levels, as well as the mineral content of leaves and fruits in terms of nitrogen, phosphorus, potassium, calcium, and iron, when compared to untreated plants [63]. The selectivity of natural and surfacemodified zeolite for NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>, as well as its ability to minimize nutrient leaching, was reported by Mondal *et al.,* [64].

#### **Table 5**

The concentration of nitrite and nitrate for leaching analysis

<b>Brassica</b>	Treatment	Leaching analysis											
family		Nitrite (ppm)						Nitrate (ppm)					
		W1	W <sub>2</sub>	W <sub>3</sub>	W4	W5	W6	W1	W <sub>2</sub>	W3	W4	W5	W6
Mustard	Standard	0	0.13	0	0.1	0.25	0	1		7	13.75	5	
Green	Low	0	0.25	0.44	0.38	0.1	0	1		17	23.75	3.75	1
	Kaolin	0	0	0	0.13	0.38	$\Omega$	1		1	3.75	3.5	
	Meta	0	0	0	0.1	0.25	$\Omega$	1		1		3.75	
	Zeolite	0	0	0	0	0.25	0	1		1		6.5	
Kale	Standard	0.925	0	0	0	0	0	14.5	10.5	136	22	35.5	0
	Low	0.025	0	0	0	0.15	0.2	13	19	19	16.5	108	3
	Zeolite	12	10.5	10.5	0	0	0	12	10.5	10.5	0	71	4
	Perlite	0.475	0	0	0	0.075	0	18	19	87.5	31	120	0

# **4. Conclusions**

In conclusion, this synthetic zeolite soil addition effectively increased mustard green and kale growth while minimizing nitrite and nitrate leaching after watering. Based on the results and subsequent deliberations derived from the analysis of mustard green growth and leaching, it has been determined that zeolite exhibits superior efficacy as a soil amendment in terms of enhancing growth and mitigating leaching, in comparison to kaolin, metakaolin, and perlite. However, other inorganic

soil amendments like kaolin, metakaolin, and perlite also show slight increments in mustard green and kale growth and the potential to reduce the leaching of nitrite and nitrate.

#### **Acknowledgement**

The authors would like to thank Universiti Malaysia Perlis and Politeknik Jeli Kelantan for providing facilities support, and Universiti Malaysia Pahang Al-Sultan Abdullah for providing financial support under grant numbers RDU223018 and PGRS220391.

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