Ecolo ecological sustainability of N utilisation and leaching in solanum lycopersicum var. cerasiforme via green synthesis of zeolite LTA

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ABSTRACT

A sustainable green synthesis of zeolite from kaolin was cooperated in soil to reduce the leaching effect for environmental sustainability. An experiment was conducted to determine the effects of cation-binding mineral zeolite on nitrogen leaching, yield, and nitrogen absorption of cherry tomatoes in a pot. There are seven distinct experimental treatments: Control High (CH); Control Standard (CS); Control Low (CL); 2g of zeolite(2gZ); 4g of zeolite(4gZ); 6g of zeolite(6gZ); and 6g of industrial zeolite (6gIZ) grown in a greenhouse with randomized design. According to the results, 6g of zeolite demonstrates the smallest significant difference between the concentration mean values of nitrite and nitrate compared to the other treatments. Regarding the average nitrogen concentration in the soil at each harvest, 6g of zeolite added to the soil has the highest value compared to other treatments. There is no significant difference in fruit weight for all treatments, but 6g of zeolite results in the highest aggregate mean weight compared to other treatments. With its capacity as a CEC, this green synthesis zeolite reduced the discharge of water from a container while increasing the average nitrogen concentration in the soil. The elevated CEC of zeolite also demonstrates an increase in cherry tomato weight.

**Keywords:** Zeolite LTA; Nitrogen; Leaching; Cherry Tomato

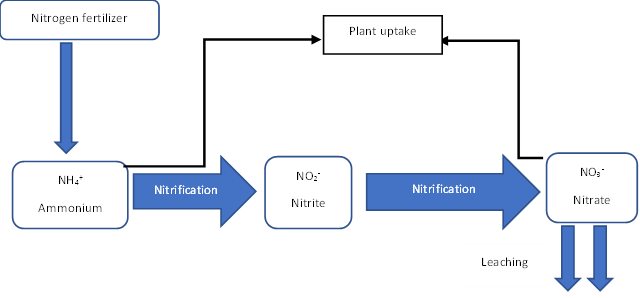
# INTRODUCTION

The tomato, scientifically referred to as Solanum Lycopersicum L., belongs to the Solanaceae family and is recognized as a highly important and popular vegetable. The cherry tomato is a widely favoured variety of table tomatoes, characterized by its diminutive size and vibrant red hue, reminiscent of a cherry. Additionally, it is renowned for its exceptional flavour [1]. The product offers essential vitamins such as A, B, C, and D, along with important minerals including calcium (Ca), phosphorus (P), and iron (Fe) [2]. A single tomato of medium size, weighing approximately 145 grams, can provide up to 40% of the recommended daily allowance (RDA) of Vitamin C and 20% of the RDA of Vitamin A [3]. The tomato belongs to the Solanaceae family, a botanical classification that designates it as a plant-vegetable fruit [4]. The tomato originated in South America and was subsequently disseminated globally by the Spaniards. Globally, the total number of tomato varieties exceeds 7,000. The Solanaceae family is widely recognized as a highly significant plant family in terms of its contribution to vegetable and fruit crops [5]. The tomato cherry, scientifically known as Solanum Lycopersicum (L.) var. cerasiforme Mill., is widely consumed as a table-purpose tomato due to its small fruit size and vibrant red colour, which closely resembles that of a cherry. Additionally, it is highly regarded for its exceptional taste [6]. This particular crop is cultivated during the duration of the warm season, necessitating substantial growth periods to maximize the yield of multiple harvests. Nevertheless, the crop with the greatest potential for successful cultivation under covered structures is the focus of attention [7]. These programs utilize the advantageous traits of cherry tomatoes in the selection of parental plants and the wide geographical range of cherry tomatoes [8]. The cultivation of cherry tomato plants within shade houses has the potential to enhance both the quality and quantity of fruit yield. The shade net house protects the crop against adverse weather conditions that could cause damage [9]. The tomatoes in question demonstrate a considerable degree of variability in various attributes related to the quality of their fruits, such as flavour, aroma, colour, and texture [10]. Currently, cherry tomatoes are cultivated in the Central American region, with substantial exports to California, Korea, Germany, Mexico, and Florida [7]. The growth cycle of a tomato plant can be divided into five distinct stages, namely germination and early growth characterized by the emergence of initial leaves within a span of 25 to 35 days, followed by the vegetative period lasting for 20 to 25 days. Subsequently, the plant enters the flowering stage, which typically lasts 20 to 30 days, followed by early fruiting within a similar timeframe. Finally, the plant reaches the mature fruiting stage, which spans 15 to 20 days [11]. The process of germination and early growth, characterized by the emergence of initial leaves, typically occurs within a timeframe of 25 to 35 days. Based on the findings of reference [11], the duration from seed planting to the initial fruit harvest can vary between 45 and 100 days, contingent upon the degree of maturity exhibited by the specific cultivar.

Nitrogen (N) is considered the most crucial among the essential elements required by plants due to its significant presence in the composition of protoplasm. N compounds account for approximately 40% to 50% of the dry matter of protoplasm [12]. The application of nitrogen (N) fertilization has been identified as a highly effective strategy for enhancing crop yield over the past six decades. N, also known as nitrogen, plays a crucial role in various growth processes of plants due to its presence in chlorophyll and numerous enzymes. The potential enhancement in crop yield resulting from nitrogen application may be attributed to an augmented synthesis of panicles in cereals and pods in legumes [13]. The application of nitrogen has been found to decrease grain sterility and enhance grain or seed weights [13]. Furthermore, the grain-to-straw ratio and harvest index of nitrogen (the uptake of nitrogen in the grain divided by the uptake of nitrogen in both the grain and straw) are positively correlated with yield in field crops and can be enhanced through the application of nitrogen [14]. Ammonium (NH4+) and nitrate (NO3) are prominent forms of nitrogen (N) that are readily accessible to plants in soil. Due to its positive charge, NH4+ exhibits limited mobility within negatively charged soils found in subtropical climates [15]. In contrast, the movement of NO3− in the soil profile is found to be six times greater than that of NH4+ when subjected to flowing water, thereby increasing the likelihood of leaching loss [16]. In conjunction with suboptimal nutrient use efficiency (NUE), the leaching of NO3− below the soil profile leads to the contamination of subterranean water sources. Several variables can influence the accumulation and transport of residual NO3− in soil. In terms of significance, it is crucial to consider the dose and timing of fertilizer application, irrigation schedule, and tillage practices. The issue of excessive NO3- levels in the soil profile can arise not only from excessive fertilization but also from a lack of synchronization between the timing of fertilizer application and the plant's stage of nutrient demand. The presence of a high concentration of nitrogen in the soil in situations where there is no crop or when the crop's demand for nitrogen is minimal, such as before emergence or at the time of harvesting, can lead to significant losses through leaching [17]. Furthermore, the leaching of NO3− appears to be more pronounced when there is a confluence of elevated NO3 levels within the soil profile and a subsequent period of intense precipitation or substantial irrigation. The practice of dividing fertilizer application and refraining from applying it during periods of heavy rainfall, such as the monsoon season, has the potential to improve nitrogen use efficiency (NUE) and mitigate losses of NO3 through leaching [18]. The leaching of NO3− to groundwater from nitrogen fertilizer is concerning. The quantity of nitrogen (N) leached through the soil profile is contingent upon the amount of nitrogen present in the soil solution and the quantity drained over a specified period. There are four primary categories of nitrogen (N) that can be found within soil: (a) N that is found within organic matter, (b) N that is a component of microbial bodies, (c) NH4+ ions that are bound to the surfaces of clay particles and organic matter, and (d) mineral forms of N, specifically NH4+, NO3−, and small amounts of NO2-, that are present within the soil solution.

The overuse of nitrogen (N) fertilizers on cultivated lands results in significant nitrogen losses through leaching. This phenomenon contributes to water pollution and escalates the expenses associated with agricultural production [19-20]. In order to satisfy the increased need for vegetables, a substantial quantity of water has been utilized for the purpose of irrigation [21], thereby exacerbating the issue of nitrogen leaching [22]. Nitrogen, a vital nutrient element for the growth of plants, undergoes processes such as mineralization and denitrification, leading to its conversion into gaseous forms. Additionally, crops can assimilate nitrogen and fixed within the organic matter in soil [23]. Additional forms of nitrogen present in soils that are not directly involved in the aforementioned processes have the potential to leach into underground water sources [24]. In contemporary times, the phenomenon of soil nitrogen leaching in cultivated land has emerged as a significant factor contributing to water pollution across various regions of China. The presence of nitrogen pollution in water bodies is intricately linked to land-use patterns and sporadic occurrences such as rainfall and soil disturbance. Furthermore, effectively managing the leaching loss of soil nitrogen poses considerable challenges [25].

Nitrogen, being the most prevalent constituent in Earth's atmosphere, exists in diverse manifestations encompassing elemental nitrogen, nitrate, and ammonia. There exist a multitude of natural and anthropogenic sources of nitrogen, all of which possess the potential to contribute to the contamination of groundwater with nitrates [26]. The generation of nitrate and ammonium ions is a consequence of inherent interactions occurring between atmospheric nitrogen and water used for irrigation, as depicted in Fig 1. The primary cause of elevated nitrate levels, posing a significant risk, can be attributed to anthropogenic activities. The three primary anthropogenic sources that make the greatest contributions are septic tanks, the application of nitrogen-rich fertilizers for turf grass, and agricultural operations [27]. The contamination of agricultural groundwater due to nitrate pollution is a widespread concern with far-reaching implications for human health, economic stability, and ecological balance. The discharge of contaminated groundwater into surface water not only results in the deterioration of potable water quality but also exerts adverse effects on aquatic ecosystems.



**Figure 1**: Nitrogen cycle

Zeolites are a type of hydrated aluminosilicate material that is formed by the interlinking of oxygen atoms between tetrahedral alumina (AlO4) and silica (SiO4) units [28]. The material in question exhibits an open void with a three-dimensional crystal structure characterized by the coordination of aluminium, silicon, and oxygen with active metals. Zeolites consist of central atoms (Al, Si, or P) and terminal oxygen atoms arranged in a tetrahedral structure, which serve as the primary building blocks. Additionally, they can form secondary building blocks by connecting through oxygen-oxygen atoms, forming rings, prisms, and structures of various sizes. Zeolites comprise a fundamental aluminosilicate framework characterized by a tetrahedral configuration of silicon and aluminium ions, each surrounded by four oxygen anions [29]. In contrast, synthetic zeolite synthesis involves applying heat to China clay, feldspar, soda ash, and other relevant sources [30]. Various categories of synthetic zeolites exist, including zeolite A, X, Y, and P, which can be produced using diverse sources [31]. Zeolites A, X, and Y are composed of a cubo-octahedral structure characterized by p-cages, wherein each corner of the framework contains tetrahedral units consisting of SiO4 – and AlO4 - ions [32]. Zeolites X and Y are widely recognized for their exceptional stability and rigid crystalline framework, characterized by significant void volume [33]. Both natural and synthetic zeolites have significant applications in various industrial, agricultural, and biomedical processes [34]. Numerous scholars have directed their focus towards the synthesis, characterization, and surface modification of zeolites, as well as exploring their various applications.

The application of zeolites in agricultural practices is feasible due to their distinctive characteristics, including cation exchange properties, molecular sieving, and adsorption [35]. Zeolites possess the ability to undergo reversible water loss and gain while maintaining their crystal structure. This characteristic has led to the proposition that zeolites could potentially serve as viable options for applications such as fertilizers, stabilizers, and chelators. For instance, a research study has demonstrated that the utilization of zeolites facilitates the gradual release of nutrients from both inorganic and organic fertilizers [36]. Zeolites exhibit significant utility in the field of agriculture due to their considerable porosity, notable cation exchange capacity, and discerning affinity towards ammonium and potassium cations. Nutrients can be transported and released by them, serving as both carriers and a medium for nutrient delivery. The primary application of zeolites in the field of agriculture pertains to the capture, storage, and gradual release of nitrogen. Previous studies have demonstrated that zeolites possess a distinct ability to selectively adsorb ammonium ions (NH4+). This characteristic enables zeolites to effectively capture this particular cation from various sources, such as farmyard manure, composts, or fertilizers containing ammonium. Consequently, the implementation of zeolites in agricultural practices can significantly mitigate nitrogen losses, thus minimizing environmental impacts [37].

Zeolites can alter soil's water content through the manipulation of bulk density and aeration porosity. In order for the nucleation process to be effective, it is necessary to establish equilibrium between the solid gel phase and the solution. The maintenance of this balance is imperative throughout the entirety of the process [38]. Zeolites have been found to enhance the water-holding capacities of sandy soils. The application of natural zeolite to the soil resulted in an increase of 0.4-1.8% and 5-15% in water-holding capacity under drought and general conditions, respectively, when compared to untreated soil [39]. It was demonstrated that sandy soil exhibited a porosity of 0.413, a bulk density of 1.66 Mg m-3, and a cation-exchange capacity (CEC) of 0.8 cmol (+) kg-1 [40]. Conversely, zeolite-treated soil displayed a porosity of 0.437, a bulk density of 1.60 Mg m−3, and a cation-exchange capacity (CEC) of 1.6 cmol (+) kg-1, according to the same parameters. Zeolites have been found to enhance water-use efficiency (WUE) through their highly porous structure, which increases both the soil's water-holding capacity and its accessibility to crops [41]. Zeolites have been found to facilitate the process of rapid re-wetting and improve the lateral movement of water towards the root zone in irrigation systems, resulting in the conservation of the requisite water for agricultural irrigation [42]. Previous research has shown that the utilization of zeolites for the exchange of ammonium (NH4+) and phosphate (P) ions, followed by the application of these ion-exchanged zeolites to the soil, can serve as an effective method for supplementing nutrients to plants [43]. This approach has demonstrated the potential to make essential plant nutrients, such as nitrogen and phosphate, more accessible to plants. The aim of the study is to investigate the effectiveness of zeolite as a soil amendment to control the leaching of nitrogen as well as very highly efficient cation exchange capacity.

# MATERIALS AND METHODS

## Synthesis of Zeolite from Kaolin

The kaolin mineral undergoes a calcination process to be transformed into metakaolin, which is subjected to heating in a furnace at different temperatures, specifically 600°C, for 4 hours. Approximately 3 grams of metakaolin were carefully weighed and added to a beaker containing 60 mL of a dilution solution of sodium hydroxide. The metakaolin was then slowly mixed with a 1M solution of NaOH. During the ageing phase, the mixture underwent continuous mixing for a duration of 24 hours at a temperature of 40°C. The amalgamation was conducted within a confined environment to mitigate the risk of desiccation caused by evaporation. After the completion of the ageing step, the solution was consistently transferred into a 100 mL Teflon-lined autoclave for the purpose of the crystallisation process. The crystallisation process was conducted at a temperature of 100°C for a duration of 9 hours. Subsequently, the mixture will be permitted to rapidly cool down in a tray immersed in cold water. Upon completion of the procedure, the liquid portion, known as the supernatant, was gathered and subjected to a series of washes until the pH of the solution decreased to a value below 8. The residual solid was subjected to thermal treatment in an oven set at a temperature of 60°C for a duration of 12 hours.

## Leaching Experiment

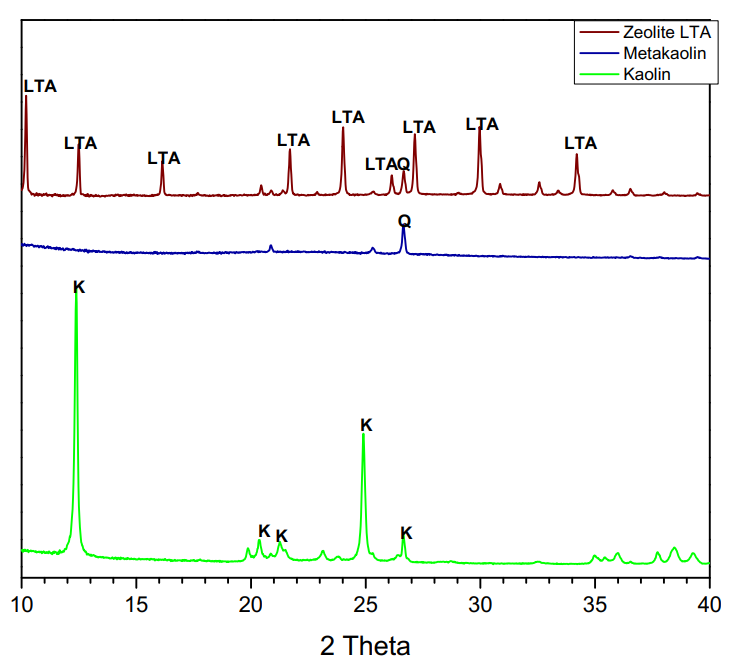
The entirety of the experiment was conducted within a controlled greenhouse environment. There are seven treatments in this experiment: Control High (CH); Control Standard (CS); Control Low (CL); 2g of zeolite(2gZ); 4g of zeolite(4gZ); 6g of zeolite(6gZ) and 6g of industrial zeolite (6gIZ). The study was conducted within the controlled environment of a greenhouse, utilizing a specific cultivar of cherry tomato known as Green World F1 Hybrid. The NPK fertilizer quantity, soil type, and watering frequency were standardized across all tomato cherry trees. The tomato cherry seed was planted in the tray and left to germinate for a period of 28 days. Following a period of 28 days from the initial sowing, the seed was subsequently transplanted into individual pots within the confines of the greenhouse. NPK green and NPK blue were applied to facilitate the growth of the leaves and the fruit, respectively. EuroCHEM is the manufacturer of Nitrophoska fertilizers, which are available in two variants: NPK green and NPK blue. The NPK green fertilizer has a composition of 15% nitrogen, 15% phosphorus, and 15% potassium, while the NPK blue fertiliser has a composition of 12% nitrogen, 12% phosphorus, and 17% potassium. The utilisation of these fertilisers was implemented in a controlled greenhouse experiment. Each experimental group of plants will receive different fertilisation rates. The control high group will be fertilised at a rate of 20g per pot, the control standard group at a rate of 12g per pot, the zeolite group at a rate of 2g per pot, the 4g zeolite group at a rate of 4g per pot, the 6g zeolite group at a rate of 6g per pot, and the industrial zeolite group at a rate of 6 g per pot. The control low group will receive a fertilisation rate of 5g per pot.

Each treatment was conducted three times. The planting soil was sourced from Kean Beng Lee Industries. The soil composition consisted of coco peat, burnt soil, river sand, burnt husk, rich humus, and charcoal powder. The dimensions of the greenhouse are 5.5 metres in length and 2.8 metres in width, while the height of the greenhouse tunnel measures 2.5 metres. The methodology employed for leachate collection entailed the placement of four identical pots for each treatment within individual plastic containers. The concentrations of nitrite, nitrate, and ammonium in the leached water were assessed through weekly collection of water samples, subsequent freezing, and subsequent analysis at a later time. At the onset of Week 1, the initial leachate sample was collected precisely 28 days subsequent to the sowing of seeds. Subsequently, systematic sampling of leach test was conducted. The nitrite and nitrate levels lost from the pots in the leachate samples were determined using ion chromatography. The samples collected from the Leaching Experiments were subjected to analysis for nitrite and nitrate using an anion exchange column. A volume of five millilitres of filtered and diluted samples, adjusted to contain an appropriate concentration of anions for detection, was introduced into the automated sampling system. Subsequently, the participants underwent a ten-minute run on the ani-on column. The concentrations of nitrite, nitrate, and ammonium ions in the leachates were determined by normalising the peak areas obtained from the ion chromatography (IC) traces to their respective calibration curves. Each result was analysed using statistical methods in order to determine the least significant differences (LSD) between the various treatments. The statistical significance of each finding was assessed using the software program SPSS, version 10 for Windows. A one-way analysis of variance (ANOVA) was conducted to analyse all plant and soil measures within each harvest. Prior to conducting the analysis, a homogeneity of variance test was conducted on the data to evaluate whether they met the necessary criteria for ANOVA. The data were analysed to determine the least significant differences (LSD) between the treatments in each experiment.

# RESULT AND DISCUSSION

## Synthesis of Zeolite Characteristics

Based on the results obtained from the particle size analysis, it was determined that the average diameter of kaolin particles was found to be 497 nm, equivalent to 0.497 µm. It was observed that the particle size range of kaolin spans from 0.4 to 0.75µm [44]. The mean diameter of zeolite, as determined at the conclusion of the analysis, is 43.8 nm, which is equivalent to 0.0438 micrometres. The unprocessed kaolin sample displayed similar X-ray diffraction (XRD) pattern to that of kaolinite, a mineral characterised by a layered structure with diffraction planes [0 0 1] and [0 0 2] at 2Ɵ values of 12.398° and 24.944°, respectively (Fig 2) [45]. The peaks displayed in Figure 2 represent the characteristic features of kaolinite. The pattern number 98-0037558 in the International Crystal Structure Database (ICSD) was observed to correspond to the sharp apex. Based on the outcomes of the investigation, it has been determined that the singular mineral predominantly observed is kaolinite, constituting 100 percent of the composition. The aforementioned ratio confers benefits to the pathway facilitating the synthesis of zeolite from refined kaolin subsequent to a form of beneficiation procedure. The aforementioned conclusion is substantiated wherein they observe that the X-ray diffraction (XRD) pattern of the initial kaolinite specimen exhibits two prominent reflections at 2θ values of 12.3° and 24.8°, as documented in the PDF card 00–058-2001 [46]. At an angular range of 2Ɵ = 20–24.5° and 2Ɵ = 35–40°, additional low-intensity reflections were observed in relation to the edge of the kaolinite crystal [47]. Following the process of calcination, the X-ray diffraction (XRD) pattern of metakaolin undergoes alterations, characterised by shifts in peak intensities within the range of 2θ = 20.861 and 26.644, specifically at a temperature of 600 °C (refer to Fig 2). The observations at temperatures of 600 °C indicate that quartz is the primary constituent [45]. The presence of ten distinct peaks at specific 2θ angles, namely 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, as depicted in Figure 2 [45], serves as an indication of zeolite production.



**Figure 2.** XRD analysis of (a) kaolin, (b) metakaolin and (c) zeolite LTA; K: kaolinite, Q: Quartz; LTA: Zeolite LTA

The hexagonal plate shape of kaolinite crystals was confirmed through the use of scanning electron micrographs, as depicted in Fig 3. The unprocessed kaolin samples display a lamellar structure in their morphologies [48]. The production of highly disor-dered metakaolin with an amorphous structure and a sheet-like shape was observed as a result of the calcination process [45,49]. Figure 3 depicts a scanning electron microscope micrograph that provides evidence of the congruence between the synthesised Zeo-lite-LTA and the cubic crystalline system family. Figure 3 depicts the observation of zeolite crystals that exhibit a high degree of crystallinity, displaying a uniform cubic morphology and consistent diameters. The cubic arrangement of the zeolite crystals was clearly evi-dent, with an average length of less than 2 µm.



**Figure 3.** FESEM analysis of (a)kaolin, (b) metakaolin and (c)zeolite

## Nitrate and Nitrite Analysis

Tables 1 and Table 2 present the mean values of nitrite and nitrate, respectively, from week 1 to week 12. The statistical analysis reveals that the average nitrate concentration at week 1 demonstrates a significant difference among all treatments when 6g of Zeolite is applied, as well as in the control group with high nitrate concentration. The control standards demonstrate the overall significance of the experiment, as all treatments were administered with a uniform dosage of 4g of Zeolite. The results indicate that there are significant differences observed among all the treatments involving nitrite. During the second week of the experiment, notable variations were observed among all treatment groups in relation to the application of 2g, 6g, and industrial Zeolite. No statistical signif-icance is observed in the control group when considering solely the control standard. Sim-ilarly, in the control low group, no statistical significance is observed when considering only 4g of Zeolite. Significant results were observed for all treatments involving nitrite, specifically with the utilisation of 2g, 4g, and industrial zeolite. During the third week of the experiment, it was observed that all treatments, including nitrate, control high, control low, 4g, 6g, and industrial Zeolite, exhibited a high level of significance. Significant results were observed for all treatments, including nitrite, control high, control standard, control low, and 6g of zeolite. In the fourth week, all treatments exhibited a statistically signifi-cant relationship with each other in terms of nitrate levels. Significant results were ob-served for all treatments involving nitrite, including the control high, control standard, 2g, 6g of Zeolite, and industrial zeolite treatments. During the fifth week, a significant differ-ence was observed among all treatments regarding nitrate levels. Significant results were observed for all treatments involving nitrite, with 2g of Zeolite, 6g of Zeolite, and industri-al zeolite demonstrating significance.

By the sixth week, it was observed that all the treatments exhibited significant differ-ences from one another in terms of nitrate analysis. A notable distinction is observed be-tween the effects of 6g of Zeolite treatment and all other treatments, with the exception of industrial Zeolite, in relation to nitrite. In the seventh week of the experiment, it was ob-served that the application of 6g of Zeolite resulted in a statistically significant effect on nitrate levels across all treatment groups, indicating its efficacy in controlling low nitrate concentrations. The experimental results indicate that nitrite, control high, control stand-ard, control low, 6g of Zeolite, and industrial zeolite exhibit statistically significant effects compared to all other treatments. In week 8, a significant difference was observed among all the treatments regarding nitrate levels. The control group exhibits statistical signifi-cance in relation to all other treatments with regard to nitrite levels. The Zeolite sample weighing 6 grams exhibited a notable statistical significance across all treatments, except for the industrial Zeolite treatment. In the ninth week of the study, it was observed that there was a significant difference in nitrate levels among the treatment groups, including the control high, control standard, and control low groups. A notable distinction is ob-served among the various treatments for the 6 grams of Zeolite, with the exception of the 4 grams treatment. A notable disparity exists among all the treatments at the nitrite stage. In the tenth week of the study, it was observed that there was a significant difference in ni-trate levels among all the treatments. Significant differences were observed among the treatments for nitrite, including control high, control standard, control low, and industrial zeolites. In the eleventh week, a significant difference was observed among all treatments concerning nitrate levels. Significant differences were observed among all treatments for nitrite levels, including the control high, control low, and 4g of Zeolite treatments.

**Table 1**. Mean concentration (mg/L) of nitrite from week 1 until 12

**Table 2**. Mean concentration (mg/L) of nitrate at week 1 until 12

The ob-served results indicate a notable distinction among the control high, control low, 2g, 4g, and industrial zeolite samples, each weighing 6g. In the twelfth week, a statistically sig-nificant difference was observed among all treatments regarding nitrate levels. A signifi-cant difference is observed in all treatments between the control high and 4g of Zeolite in terms of nitrate levels. The experimental results indicate a notable distinction among the control high, control standard, control low, and 4g of Zeolite samples with respect to the observed 6g of Zeolite.

The mean concentrations (mg/L) of nitrate and nitrite from week 1 to week 12, as presented in Table 1 and Table 2, have been graphically depicted in Figure 4. The figure provides a comparison of the mean nitrite concentrations (mg/L) for each treatment group: (1) control high, (2) control standard, and (3) control. The experiment involved the use of different amounts of zeolite, specifically 2g, 4g, 6g, and industrial zeolite. The study also included control groups with high, standard, and low levels of zeolite. The results are presented in Figure 5, which depicts the mean nitrate concentration (mg/L) for each treatment over the course of several weeks.



The process of altering natural Zeolite involves initial preparation through grinding and screening, followed by subsequent modification using sodium salt [50]. This modification induces alterations in the pore size and surface area of Zeolite, resulting in an enhanced capacity for ammonium ion absorption. The application of zeolite to soil has been found to enhance the utilisation efficiency of nutrients. These factors facilitate comprehension of the function that Zeolite fulfils in this process. Previous studies have provided evidence that incorporating zeolite into soil, in conjunction with applying chemical fertilisers, leads to a decrease in nitrogen leaching [51]. Furthermore, it has been observed that this phenomenon decelerates the mineralization process, resulting in a gradual release of nutrients. Additionally, it has been found to have the capacity to decrease the amount of Nitrogen lost through volatilization [52]. The transient nature of ammonium ions within the cavities and lattices of Zeolite facilitates their efficient transfer to plants as needed. The application of zeolite treatments has been found to result in a decrease in both nitrification and leaching losses [53-54]). The gradual depletion of nutrients from the topsoil is a well-documented phenomenon. However, zeolites possess the capacity to effectively retain these essential nutrients within the soil matrix, thereby preventing their loss. As a result of this phenomenon, farmers are capable of decreasing the quantity of fertiliser they administer to their agricultural plots, resulting in a concomitant decrease in the overall expenditure associated with crop cultivation [55]. The compounds under investigation have demonstrated exceptional selectivity and capacity for the sorption of NH4+ ions. This can be attributed to the electrostatic interactions that occur between the positively charged NH4+ ions and the negatively charged sites within the zeolite structure. The reason for this phenomenon can be attributed to the elevated cation exchange capacity (CEC) exhibited by zeolitic minerals [56]. The strong attraction between zeolites and NH4+ cations can be effectively utilised to enhance the control of the retention and release of this cation in soil media [57].

Conversely, the incorporation of zeolites into soils has the potential to augment the adsorption capacity of NH4+ within the soil matrix. This phenomenon can be attributed to the strong affinity of zeolites for the entrapment of NH4+ molecules via ion exchange mechanisms. The addition of zeolites to soils has been observed to affect the retention of NH4+ by zeolitic minerals, with this retention being influenced by various factors. These factors include the Si/Al ratio, the mobile and exchangeable cations in the zeolites, the pore size and structure of the materials, pH levels, contact time, temperature, and the concentration of other ions in the soil and water. The cation exchange capacity (CEC) of certain naturally occurring zeolites surpasses that of other minerals commonly found in soils by a factor of two to three. This discrepancy can be attributed to the diverse range of zeolites, which exhibit variations in their cage structures, inherent structural defects, adsorbed ions, and associated minerals [58]. Furthermore, zeolites have been extensively utilised in conjunction with other substances to enhance the accessibility of soil nutrients, promote plant growth, and increase agricultural productivity. For example, it was observed that the combined application of clinoptilolite zeolite and fly ash to a coarse loamy soil led to a more significant enhancement in the concentration of exchangeable soil nitrogen (primarily NH4+, NO3- was not detected), in comparison to the separate application of these components. This phenomenon was observed in a conducted study. A significant improvement in the physical properties of soils and a substantial shift in cation exchange capacity (CEC) can be attributed to numerous positive impacts [59].

Consequently, the application of zeolite amendments has the potential to significantly impact the reduction of NH4+ leaching [60]. The addition of 0.2% of clinoptilolite Zeolite by weight to a loamy soil has been found to effectively inhibit the leaching of NH4+ when exposed to incoming water. The efficacy of NH4+ absorption can be attributed to the clinoptilolite Zeolite. The introduction of clinoptilolite Zeolite, even in small quantities, to soils with sandy and loamy compositions led to a significant reduction in the levels of NH4+ . The notable high cation exchange capacity (CEC) and noticeable selectivity exhibited by various zeolites, including natural clinoptilolite and synthetic zeolite, towards plant nutrients, particularly NH4+, can be effectively utilised in the formulation of fertilisers aimed at enhancing the soil's ability to retain essential nutrients. This can be achieved by augmenting the capacity for NH4+ retention. This objective can be achieved by promoting a systematic and gradual release of these elements, which is synchronised with the plant's uptake of nutrients [61]. Due to its negative charge, the NO3- ion typically exhibits limited attraction towards soil particle surfaces and does not readily undergo adsorption in soil. However, there have been documented instances of NO3- sorption occurring on specific acidic soil types. The application of a fertiliser containing anions, such as KNO3, to soil has been found to have the potential to cause an increase in nitrogen loss and a decrease in nitrogen usage efficiency (NUE). This can be attributed to the repulsion between the NO3- anions and the soil surface [62]. The incorporation of clinoptilolite zeolite into sandy soils has been observed to result in a decrease in the leachate nitrogen concentration, as well as an increase in soil moisture and nutrient content. The observed outcome can be attributed to the increased surface area of the soil and its enhanced cation-exchange capacity [63].

An additional salient characteristic of zeolites, which renders them suitable for applications in separation and purification, is their inherent ability to offer substantial internal space volume [64]. The addition of Zeolite to soil has the potential to initially immobilise NH14N within the soil, thereby restricting the availability of nitrogen to the crop and adversely affecting its growth [54]. Furthermore, the presence of these minerals not only leads to the accumulation of substantial quantities of ammonium ions but also results in disturbances to the nitrification process when compared to Zeolite and straight urea (46% N) [65]. Zeolites exhibit a notable affinity for ammonium NH4+ ions, enabling them to effectively adsorb this specific cation from various sources such as farmyard manure, composts, and fertilisers containing ammonium. Consequently, zeolites have the potential to mitigate the environmental loss of Nitrogen. Previous studies have provided evidence to support the notion that zeolites charged with ammonium ions possess the ability to enhance the dissolution of phosphate minerals. This phenomenon has been observed to have a positive impact on agricultural productivity by increasing crop yields and facilitating the absorption of phosphorus. The research examined the solubility and cation-exchange interactions in mixtures of rock phosphate with NH4+ and K+ saturated clinoptilolite [66]. The study's findings indicate that combinations of zeolite and phosphate rock can offer gradual nutrient release to plants in artificial soil environments through dissolution and ion exchange reactions.

## Residual N in Soil at Harvest 1, 2 and 3

According to the data presented in Table 3, it can be observed that during harvests 1 and 3, the application of 6g of Zeolite exhibits a statistically significant difference when compared to all other treatments. During the second harvest, a notable distinction was observed between the experimental group treated with 6g of Zeolite and all control groups, including those subjected to high, standard, and low conditions. The mean concentration of Nitrogen at harvests 1 and 2 indicates that the treatment involving 6g of Zeolite exhibits a higher value compared to the other treatments. The zeolite possesses cations that are interconnected by relatively weak bonds, allowing for the facile modification of their aluminosilicate structure [67-68]. Zeolite possesses the inherent capability to effectively bind nutrients, thereby impeding their loss through leaching and facilitating their gradual uptake by plants [69]. This implies that there is potential for enhancing land productivity [68]. Zeolite exhibits a notable electrostatic property characterised by a consistent negative charge on its surface. This unique feature enables zeolite to possess a substantial capacity for adsorbing cations, including but not limited to potassium, ammonia, calcium, sodium, and magnesium ions, as well as numerous other cations [70]. In the context of zeolites, the interconnected three-dimensional pore structures are interlinked and give rise to elongated and broad channels, which effectively enable the facilitated transport of ions and molecules across the structures [42]. In addition, they function as a provider of certain nutrients and play a crucial role in the transportation, stabilisation, and regulation of mineral fertilisers [71]. By acting as carriers for nitrogen and potassium fertilisers, they enhance the efficiency of these fertilisers, enabling reduced application rates without compromising yield levels. The impact of Zeolite on nitrogen uptake and plant growth would differ depending on the soil type, with the most significant potential for positive outcomes observed in soils characterised by a coarse texture and a low cation exchange capacity (CEC) [72]. The impact of Zeolite on nitrogen uptake and plant growth would differ depending on the type of soil [72]. Specifically, it was hypothesised that soils with a coarse texture and low cation-exchange capacity would experience the greatest benefits from the application of Zeolite.

Zeolites exhibit structural similarities to honeycombs or other cage-like formations, characterised by their substantial void spaces or cavities. The presence of aluminium generates a negative charge, necessitating the counterbalancing of cations with a positive charge. Zeolite can retain and store essential nutrients within the root zone, enabling plants to access these nutrients as and when required. Consequently, this leads to enhanced utilisation of nitrogen (N) and potassium (K) fertilisers, which can be achieved through the reduction of their application rates while preserving the equivalent crop yield, prolonging their duration of effectiveness, or alternatively, by generating higher crop yields. As a consequence of this phenomenon, utilizing zeolites is anticipated to yield enhanced plant growth and development through reducing nutrient loss. The zeolite mineral deposits in their natural state are characterised by the presence of exchangeable cations such as calcium (Ca2+), magnesium (Mg2+), potassium (K+), and sodium (Na+). Zeolite has the ability to replace various cations with NH4+ and other metal cations, depending on the pH value of the solution and the concentrations of these cations [73]). The partial substitution of Si4+ by Al3+ results in the generation of an excess of negative charge. The surplus of negative charge is counterbalanced by alkali and earth-alkaline cations [74]. Furthermore, apart from the water molecule, these cations are distributed throughout the cavities and channels within the aluminosilicate macro anion framework [75]. The potential exists to eliminate the water molecule in an alternative manner or replace it with alternative sorbates. Modified zeolite can be obtained for specific applications, such as removing NH4+ and hazardous metal cations from wastewater, through substituting metallic cations in the crystalline structure [76]. This process can be achieved through the substitution of metallic cations with alternative cations [74]. Zeolites possess the capacity to adsorb a wide range of polar and non-polar inorganic or organic molecules within the cavities or channels of their structural framework [74].

**Table 3.** Mean concentration (mg/L) of nitrogen in the soil at harvests 1,2 and 3



## Yield of Cherry Tomato

No statistically significant difference was observed among the various treatments (Table 4). However, the fruit weight of the treatment amended with 6g zeolite exhibited the highest weight in comparison to the other treatments incorporated into the soil. During the second harvest, it was observed that the addition of 6g of Zeolite resulted in a 21.38% increase in the weight of cherry tomatoes compared to the low control group. In comparison to other treatments, the percentage difference in cherry tomato weight ranged from 7% to 16%. During the third harvest, it was observed that the weight of cherry tomatoes increased by 18.31% and 18.51% when treated with 6g of Zeolite, in comparison to the control group treated with a low amount of Zeolite (3g) and a higher amount of Zeolite (4g), respectively. The application of Zeolite to soil, in conjunction with synthetic or organic fertilisers, has been observed to increase crop yields across various crop types. This improvement in crop productivity can be attributed to the positive effects on soil structure and nutrient conditions brought about by Zeolite application [77].

**Table 4.** Cherry tomato yield(g) at harvest 2 and 3



# CONCLUSIONS

Managing the nitrogen fertilizer application in the field is one of the most effective methods for preventing nitrate contamination of groundwater. The results of this study suggest that 6g of zeolite amended in soil could reduce nitrate leaching, improve nitrogen uptake of cherry tomatoes, and improve environmental sustainability. The zeolite levels applied in this greenhouse study result show significantly different effects on the leaching of nitrate and nitrite in groundwater. The capability of zeolite with a high cation exchange capacity increases the binding site of zeolite with N ion. The fruit weight did not show a significant difference with all treatments, but 6g of zeolite showed the highest mean fruit weight for harvest 2 and 3 compared to other treatments.

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