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Effects of Soil Treatments and Grinding on Nutrient Availability in Halloysite-Rich Soils from Djando Plateau, Mohéli

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Abstract

This study examines the impact of soil treatments and grinding on the chemical reactivity, mineral structure, and nutrient availability of halloysite-rich soils from the Djando Plateau, Mohéli, Comoros, after 20 years of pesticide exposure. The research evaluates three soil amendments—sulfur dioxide (SO_2), calcium hydroxide $Ca(OH)_2$, and untreated soil—focusing on their effects on potassium (K) extraction and soil pH over time. The results indicate that grinding and chemical treatments significantly modify the soil's mineral composition and reactivity. Fourier transform infrared (FTIR) spectroscopy reveals that untreated soil maintains its original mineral structure, while grinding alters hydration states and hydroxyl group coordination. X-ray diffraction (XRD) analysis shows that grinding, particularly when combined with sulfur treatment, disrupts crystal structures, enhancing soil reactivity by increasing surface area and ion-exchange capacity. Additionally, SO_2 and $Ca(OH)_2$ applications raise soil pH and improve potassium availability, with $Ca(OH)_2$ having the most pronounced effect. These modifications enhance nutrient solubility, potentially improving soil fertility and agricultural productivity. The study highlights the role of soil amendments, especially $Ca(OH)_2$, in optimizing soil chemical properties and supporting sustainable agriculture.

Keywords

Halloysite-Rich Soil, Mohéli, Comoros, Pesticide Contamination, Soil

Amendments, Nutrient Availability, Agricultural Management

1. Introduction

The soil quality in Djando, located on the island of Mohéli in the Comoros, plays a crucial role in supporting local agricultural practices. Agriculture is a vital activity for local communities, with staple crops such as maize, cassava, and rice, as well as commercial crops like cotton and coffee. While traditional farming methods remain predominant, the use of chemical inputs, particularly pesticides, has increased in recent decades in response to pest and disease pressures. This shift has led to significant changes in soil health, as chemical interventions alter its physical, chemical, and biological properties [1]. These transformations raise particular concerns on the Djando Plateau, where soils rich in halloysite, an aluminosilicate clay mineral, are widespread. Halloysite-rich soils have attracted growing interest due to their unique properties, including a high surface area, high cation exchange capacity, and the ability to adsorb various substances, including pesticides. The mineral structure of halloysite, characterized by 2:1 phyllosilicates, is particularly well-suited for potassium adsorption and other nutrients, thereby enhancing soil fertility [2]. However, these same properties make halloysite-rich soils highly susceptible to disruptions caused by prolonged pesticide use. Repeated applications of these substances can alter soil chemical reactivity, nutrient availability, and microbial diversity—key factors in maintaining long-term soil fertility [3]. Studies have shown that pesticides such as chlorpyrifos reduce earthworm biomass and disrupt essential enzymatic activities, thereby compromising microbial communities crucial for soil health [4]. Additionally, pesticides decrease the abundance and diversity of soil fauna, affecting nutrient cycling and the overall functioning of soil ecosystems [5].

The extensive use of pesticides worldwide has been linked to various detrimental effects on biodiversity and soil fertility [6]. While these substances have effectively controlled pests and increased agricultural yields, their excessive and prolonged use has contributed to soil degradation by disrupting microbial biomass and biodiversity essential for soil health [7]. This disruption is particularly evident on the Djando Plateau, where pesticide exposure has led to persistent soil contamination. The presence of heavy metals in the region, likely linked to pesticide use, fertilizers, and poultry manure, further complicates the situation [8]. Moreover, the impact of these chemicals extends beyond their toxicity to living organisms, affecting the mineralogical structure of the soil [9]. Prolonged pesticide exposure has been shown to induce changes in mineral crystallinity, leading to the amorphization of certain mineral phases, which in turn affects the soil's ability to retain and release essential nutrients [10].

In response to these challenges, this study aims to evaluate the effects of prolonged pesticide exposure on halloysite-rich soils in Djando, focusing on the mineralogical and chemical transformations induced by these substances. A novel process for extracting potassium from halloysite-rich soils has been developed using dry grinding with calcium hydroxide $Ca(OH)_2$ or sulfur (SO_2), with potassium dissolution controlled through two methods. This approach will enable the analysis of structural modifications in the soil, particularly its chemical reactivity and nutrient retention capacity. The data collected will provide valuable insights into the long-term impacts of pesticide use on soil quality and contribute to the development of more sustainable agricultural practices that balance soil health preservation with local agricultural productivity.

2. Materials and Methods

2.1. Transition from Historical Method to New Method

Historically, the use of pesticides on the Djando Plateau in Mohéli, Comoros, has led to soil contamination, especially with high pesticide doses applied over the last 20 years. As summarized in **Table 1**, this practice has resulted in significant environmental consequences, including soil degradation, biodiversity loss, and a decline in agricultural productivity. Despite this, agricultural practices continued with some improvements under the supervision of international assistance, but the long-term impact of pesticide overuse has prompted the need for a more sustainable solution.

Table 1. History and use of pesticides in the Djando Plateau Region, Comoros [11] [12].

Period	Key Events	Consequences	Actors and Issues
1980s	Introduction of pesticides through the Japan-Comoros cooperation project (KR2 Project).	Increased pesticide uses in agriculture.	Compliance with dosage standards, but no studies on soil composition before using chemicals.
Current Situation	Pesticides mainly used in vegetable farming, less so in subsistence agriculture.	Increased soil contamination and biodiversity deterioration.	Insufficient control and regulation, with some farmers reusing pesticide leftovers without adhering to norms.
Current Problem	Overuse of chemicals without monitoring and poor management of pesticide leftovers.	Negative impact on soil health and local ecosystems.	Noticeable decline in production in government-supervised projects.
2019-2024	Decline in production in government projects: 50% - 46% (compared to 90% previously).	Decreased agricultural yields.	Farmers facing difficulties due to high costs and polluting effects of chemical fertilizers.
Proposed Solution	Researching alternative methods to repair soils and improve agricultural yields.	Improved soil quality and increased yields.	A desire to reduce chemical use and explore more ecological alternatives (Nguyen and Lee, 2017).

The decline in soil health and the significant reduction in agricultural yields led to the exploration of new techniques for soil rehabilitation. As shown in **Table 2**, local agricultural input distribution is still centralized, with a limited number of outlets for chemical products. This situation underlines the necessity of moving towards more sustainable practices and reducing dependency on chemical inputs.

Table 2. Distribution network of agricultural inputs in Comoros.

Islands	Number of Sales Points
Ngazidja (Grande Comore)	22 sales points
Anjouan (Ndzouani)	9 sales points
Mohéli (Mwali)	1 sale points

2.2. Halloysite-Rich Soil Remediation Approach

In response to the issues highlighted by the historical pesticide use, a new method was developed to address the contamination of the soils on the Djando Plateau. The primary objective was to repair the damaged soil and restore its fertility to increase agricultural yields. The method involves using halloysite-rich soils that have been impacted by high pesticide doses over the past 20 years from the Djando Plateau in Mohéli, Comoros, were carefully collected, with over 6 kilograms of soil sampled from a depth range of 0 to 40 cm. The samples were then analyzed using the method in our previous publications [13], (Said, Hu *et al.* 2021). For the analysis, 2.0 g of halloysite powder was milled in a planetary ball mill (Pulverisette-7, Fritsch, Germany), equipped with two zirconia pots (45 cm^3 internal volume) containing 7 zirconia balls, each 15 mm in diameter. The milling time ranged from 0 to 180 minutes, while the rotational speed was fixed at 600 rpm. The halloysite powder was mixed with SO_2, and separately, with $Ca(OH)_2$. To evaluate the release characteristics, a 2% citric acid solution (Sinopharm Group Co Ltd., Shanghai, Analytical reagent) was used. In each experiment, 0.02 g of the milled soil (or soil mixed with SO_2 or $Ca(OH)_2$ was dispersed in 100 ml of distilled water or citric acid solution, respectively. The mixture was stirred on a magnetic stirrer (524 G, Meiyingpu Shanghai, China) for 120 minutes at 500 rpm under room temperature. The pH of the solutions was measured using a pH meter (Seven Compact, Mettler Toledo, Switzerland). The suspension was then centrifuged to remove the solids, and the concentration of potassium in the supernatant was measured using Atomic Absorption Spectrometry (AA 6880, Shimadzu, Japan) to calculate the K extraction rate. X-ray diffraction (XRD) characterization of the prepared samples was performed using a MAX-RBRU-200B diffractometer (Rigaku, Japan). Fourier Transform Infrared (FT-IR) spectra were recorded over the range of 4000 - 450 cm^{-1} using a Nicolet 6700 spectrometer (Thermo Fisher, USA), with KBr as a diluent.

3. Results and Discussion

3.1. Chemical Composition of Halloysite Soil

The halloysite soil is distinguished by a notable chemical composition, with proportions of 33% SiO_2, 28% Al_2O_3, and 18% Fe_2O_3 listed in **Table 3**, reflecting its richness in silicate and aluminosilicate minerals. These elements play a crucial role in the soil's reactivity and its ability to adsorb pesticides. Additionally, the content of K_2O (2.5%) and CaO (1.3%) indicates that the soil contains a moderate amount of nutrients. The loss on ignition (LOI) of 19% suggests a significant presence of organic matter in the soil. The interaction between the soil's chemical composition and the prolonged application of pesticides influences nutrient availability and the overall reactivity of the soil. Pesticides typically come into contact with the soil, where they undergo various transformations, creating a complex pattern of metabolites [14]. Proper management of these factors is crucial to prevent excessive acidification and minimize long-term contamination risks.

Table 3. The chemical composition of halloysites.

Compound	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MgO	Loss on Ignition
(wt.%)	33	28	18	2	0.1	2.5	1.3	4.2	19

3.2. XRD Characterization of Natural Halloysite from the Comoros

The XRD peaks observed for the natural halloysite sample from the Comoros correspond to the planes (001), (100), (002), (110), and (300), which are consistent with the ICDD reference 00-029-1487 [15] are shown in **Figure 1**. These results align well with the reference data, although intermediate peaks may be less pronounced or slightly shift due to geological variations and extraction methods. Notably, the peaks at $2\theta = 12.0^\circ$ and 20.1°, associated with the (001) and (100) planes, confirm an interlayer spacing of 0.73 nm for the dehydrated form and 0.44 nm for the hydrated form, similar to the halloysite reported in the literature [16].

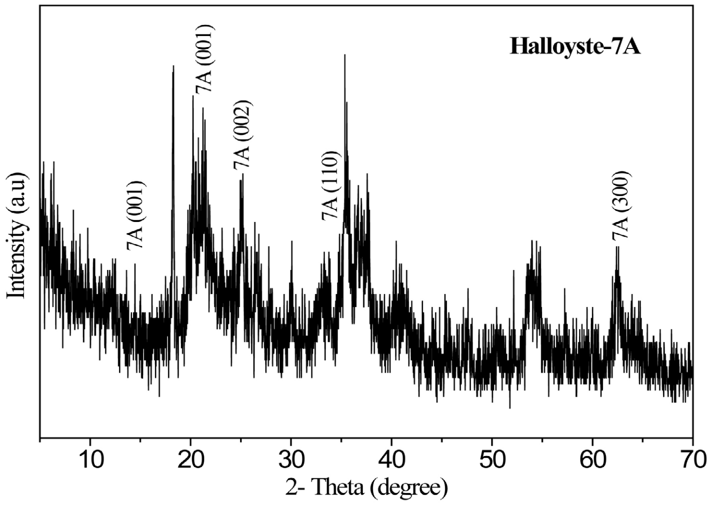
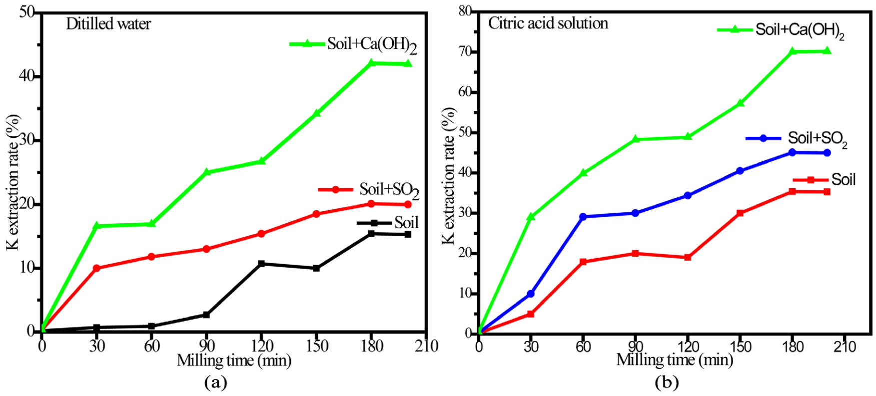


Figure 1. XRD diffraction pattern of natural halloysite from the Comoros.

3.3. Impact of Soil Amendments on Potassium Extraction Efficiency

The analysis of soil samples in distilled water and 2% citric acid, combined with varying milling durations, provided valuable insights into potassium (K) extraction (**Figure 2**). The data indicate that potassium extraction efficiency increases progressively with milling time, reaching maximum levels after 180 minutes in both media. In distilled water (**Figure 2(a)**), untreated halloysite soil showed limited potassium extraction, ranging from 0% to under 5%, suggesting minimal potassium solubilization. Adding SO_2 resulted in a moderate increase in extraction, reaching approximately 10%, indicating a minor role of sulfur in altering the soil's mineral composition. In contrast, calcium hydroxide $Ca(OH)_2$ treatment led to a significant enhancement in potassium extraction. Starting at 15%, it reached 34% after 180 minutes, which can be attributed to the alkalizing effect of $Ca(OH)_2$. This pH modification promotes the dissolution of potassium-bearing minerals, a phenomenon observed by [17].



(a) (b)

Figure 2. Potassium extraction efficiency from halloysite soil under different treatments over griding time.

The trends observed in citric acid (**Figure 2(b)**) followed a similar pattern to those in distilled water, but with considerably higher extraction rates. Untreated soil in citric acid showed an increase from 3.6% to 24.5% over 180 minutes, likely due to the soil's limited buffering capacity and increasing reactivity. The addition of SO_2 in citric acid accelerated potassium extraction, rising from 3.7% to 32.5%. This can be linked to sulfur's catalytic effect on potassium mineral dissolution, as highlighted by [18] However, the $Ca(OH)_2$ treatment outperformed the others, showing a rapid increase from 3.8% to 60% within 150 minutes and peaking at 70% after 180 minutes. This substantial improvement is due to the neutralizing effect of $Ca(OH)_2$, which reduces soil acidity and promotes potassium release, a phenomenon also noted by [19].

Regarding the milling duration, it was observed that extending the grinding time beyond 180 minutes resulted in a decrease in potassium extraction efficiency. This phenomenon can be attributed to the formation of ultra-fine particles, which, by increasing the soil's specific surface area, promote the re-adsorption of released potassium, thereby reducing its immediate availability. This behavior is crucial for establishing a connection with field conditions, where natural cycles of weathering and dissolution influence nutrient availability over extended periods. These findings highlight the importance of soil amendments, particularly $Ca(OH)_2$, in enhancing potassium availability. Furthermore, the increased potassium extraction in the presence of citric acid indicates that mineral dissolution mechanisms are strongly influenced by pH variations and cation complexation. The application of these treatments thus represents a promising strategy for optimizing soil fertility, especially in regions where potassium availability is a limiting factor for agricultural productivity.

3.4. Soil Properties and Fertility: "Influence of Texture, Nutrient Retention, and pH on Agricultural Suitability"

Table 4 summarizes soil properties from various samples, highlighting differences in texture, nutrient availability, and pH levels. Sandy soils (S_1 and S_5) show lower cation exchange capacity (CEC) and poorer nutrient retention, which makes them less suitable for sustained agriculture without regular fertilization. In contrast, silty (S_2, S_5) and clayey soils (S_3) exhibit higher CEC, allowing them to retain more essential nutrients like calcium (Ca) and magnesium (Mg), promoting plant growth [19] [20] (Bolan *et al.*, 2023). Soil pH ranges from slightly acidic to neutral (4.9 - 6.1), with slightly acidic soils typically providing optimal conditions for nutrient uptake (Takahashi *et al.*, 2001). Organic carbon is more abundant in silty and clayey soils, fostering enhanced biological activity and better water retention [21]. Silty soils display moderate acidity, while clayey soils require management due to higher acid saturation. These results indicate that silty and clayey soils offer better long-term fertility, while sandy soils require more intensive nutrient management and fertilization to maintain productivity [22].

Table 4. Physico-chimical properties of soil samples with varying textures.

Sample	Soil Texture	K (cmol (+) kg^{-1})	Mg (cmol (+) kg^{-1})	Ca (cmol (+) kg^{-1})	CEC (cmol (+) kg^{-1})	pH	Organic Carbon (%)	Total Acidity (cmol (+) kg^{-1})	Acid Saturation (%)
S_1	Sandy (60%)	0.11	0.28	0.76	1.70	5.4	O.6	0.23	16%
S_2	Silty (45%)	0.08	0.53	1.01	2.04	5.7	1.4	O.14	13%
S_3	Clayey (35%)	0.16	0.83	2.23	4.02	6.1	0.7	0.26	22%
S_4	Sandy (70%)	0.09	0.21	0.70	1.3	4.9	0.7	0.12	17%
S_5	Silty (50%)	0.07	0.38	1.4	2.60	5.4	1.3	0.21	14%

Table 5 shows that the soils have a low cation exchange capacity (average 2.33 cmol (+) kg^{-1}), indicating limited nutrient retention. The average pH of 5.5 suggests moderately acidic conditions, which can affect nutrient availability. Organic carbon content is relatively low (0.94%), reflecting limited organic matter. Total acidity remains low (0.192 cmol (+) kg^{-1}), but the acid saturation level (16.4%) may still impact soil health. Overall, these properties highlight the need for soil amendments to enhance fertility and structure.

Table 5. Statistical summary of soil chemical properties (samples S_1 to S_5).

Sample	CEC (cmol (+) kg^{-1})	pH	Organic Carbon (%)	Total Acidity (cmol (+) kg^{-1})	Acid Saturation (%)
S	S_1-S_5	S_1-S_5	S1-S_5	S_1-S_5	S_1-S_5
Min	1.3	4.9	0.6	0.12	13
Max	4.02	6.1	1.4	0.26	17
Average	2.33	5.5	**0.94**	0.192	16.4
Std Dev	1.06	0.44	0.38%	0.056	3.20

3.5. X-Ray Diffraction Analysis of Halloysite: Structural Insights and Applications

Figure 3 displays the phase transformation of halloysite with milling time (0 min, 90 min, and 180 min). X-ray diffraction (XRD) analysis of soil samples subjected highlights the progressive changes in the mineral structure caused by mechanical grinding. At 0 minutes (unprocessed soil): The XRD patterns exhibit well-defined peaks corresponding to the crystallographic planes of halloysite (001, 002, 110, and 300), indicating a well-organized structure with a high degree of crystallinity. This observation aligns with previous studies describing halloysite as a tubular mineral that remains structurally stable in the absence of mechanical stress [15]. 90 minutes of grinding: A significant reduction in peak intensity is observed, suggesting partial amorphization of the mineral structure. This attenuation is directly related to particle size reduction and the introduction of crystallographic defects due to repeated mechanical impacts. Similar findings have been reported in studies on the mechanical activation of clays [23]. At 180 minutes of grinding: The XRD peaks become increasingly diffuse, indicating an advanced state of amorphization. This trend suggests extensive disruption of halloysite's crystalline structure, making the minerals more reactive to chemical transformations and ion exchange processes. [24] have documented similar observations regarding the effects of prolonged grinding on the reactivity of clay minerals.

The progressive breakdown of the crystalline structure suggests that prolonged grinding increases the material's surface area and chemical reactivity, Similar results have been reported in studies on the mechanical activation of phlogopite mineral [25]. This transformation is particularly relevant for agricultural and environmental applications, as it can enhance the availability of nutrients previously trapped within the mineral matrix. Unlike previous findings that involved chemical amendments, these results indicate that grinding alone is sufficient to induce significant structural modifications in the soil, potentially facilitating the release of nutrients such as potassium without the need for additional chemical treatments [13]. The increasing structural disorder may also affect soil interactions with biological agents, particularly by altering nutrient adsorption capacity and influencing microbial dynamics [26].

In agricultural contexts, this approach could be leveraged to enhance the efficiency of natural fertilizers, particularly by promoting the release of potassium and other essential elements without excessive reliance on chemical amendments.

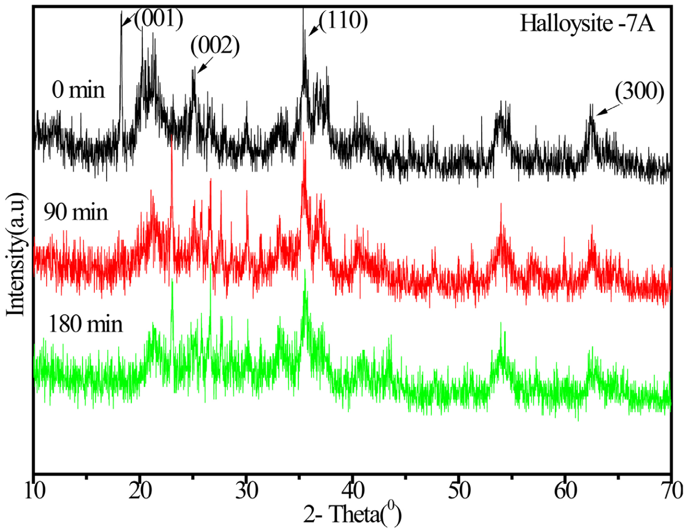


Figure 3. XRD patterns of halloysite milled at 0 min, 90 min, 180 min for 500 rpm.

3.6. pH Value in Soil Treated with SO_2 and $Ca(OH)_2$ during Grinding

Figure 4 illustrates the evolution of soil pH during grinding with three treatments: unamended soil, soil mixed with SO_2, and soil mixed with $Ca(OH)_2$ in distilled water at different milling minutes, indicating moderate acidification. This suggests limited buffering capacity, likely due to pesticide degradation over the past 20 years [27]. In contrast, soil mixed with SO_2 shows a more pronounced pH increase, rising from 2 to 6.2 over 180 minutes, likely due to sulfur neutralizing soil acidity. This pH range aligns with optimal conditions for most plants (QDEHP, 2017) [28]. The $Ca(OH)_2$ treatment results in the highest pH increase, from 4.5 to 7.6, due to its strong alkalizing effect. The reason may be highly alkaline conditions, silica dissolves further as $Si(OH)_4$, and aluminum may form soluble complexe. The dissociation of $Ca(OH)_2$ releases hydroxide ions, neutralizing acidity and improving soil conditions [29]. These results suggest that $Ca(OH)_2$ is highly effective in raising soil pH, with SO_2 providing a more gradual pH increase. Overall, these treatments significantly alter the soil pH, which in turn affects chemical reactivity and nutrient availability [30]. Under acidic or neutral conditions, halloysite slowly dissolves in water, leading to the formation of aluminum hydroxide ($Al(OH)_3$) and silicic acid ($SiO_2 \cdot xH_2O$), as shown in **Figure 4** [30]. This suggests that Equation (1) cannot adequately explain the observed phenomena.

$$mAl_2SiO_3(OH)_4 + nH_2O = 2\ m\ Al(OH)_3 + 2\ m\ SiO_2 \cdot sH_2O. \qquad (1)$$

In contrast, the reaction between the aluminosilicate $Al_2Si_2O_5(OH)_4$ and $Ca(OH)_2$ can lead to the formation of calcium silicate hydrates (C-S-H) and aluminate compounds, which are commonly observed in pozzolanic reactions [30]-[32]. This general reaction can be written as follows (2):

$$mAl_2Si_2O_3(OH)_4 + nCa(OH) = xCaO{\cdot}ySiO_2{\cdot}zH_2O + Al(OH)_3 \quad (2)$$

This reaction is particularly relevant in cement chemistry and soil stabilization, where calcium hydroxide reacts with silicate and aluminate phases to form hydrated compounds that enhance the mechanical properties of materials [30].

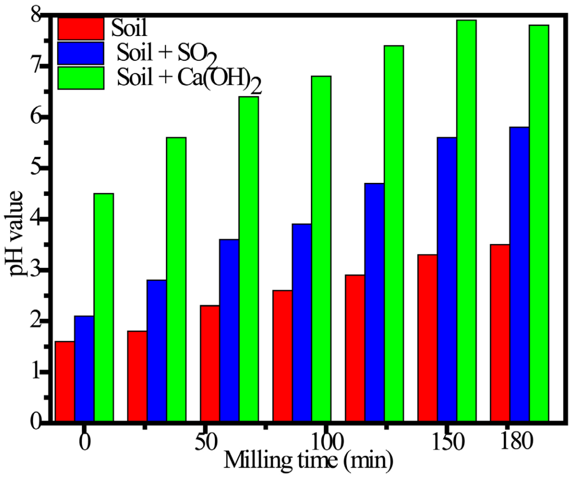


Figure 4. pH evolution over 180 minutes of grinding for untreated soil, SO_2-treated soil, and $Ca(OH)_2$-treated soil.

3.7. Impact of Pesticides and Soil Treatments on Crop Yields

The data in **Table 6** show the production of cassava, tomato, and yam in two zones (inner and outer) of rectangular plots. Cassava yields are higher in both zones (4377 kg in the inner zone and 5879 kg in the outer zone), suggesting it is less affected by pesticides or benefits more from soil treatments [33]. Tomato yields are lower in the outer zone (2233 kg) compared to the inner zone (3897 kg), likely due to the harmful effects of pesticides on soil fertility. No yam yield is recorded in the inner zone, possibly due to nutrient deficiencies from pesticide use, whereas the outer zone shows a modest yield (1384 kg), indicating yam's sensitivity to nutrient management. Pesticides disrupt soil chemistry, leading to nutrient blockages, particularly potassium [34]. Laboratory treatments with SO_2 and $Ca(OH)_2$ improved potassium extraction (32.5% with SO_2, 70% with $Ca(OH)_2$), boosting nutrient availability. These treatments also raised the soil's pH, enhancing mineral extraction and nutrient solubility, which led to higher yields of cassava and tomatoes in treated areas.

3.8. Impact of Soil Zones and Treatments on Crop Yields

Figure 5 illustrates the inner and outer zone by kg/ha. The graph clearly shows that yields are generally higher in the outer zone. Cassava yields are higher in the outer zone (979.83 kg/ha) compared to the inner zone (875.4 kg/ha). In contrast, tomato yields are slightly higher in the inner zone (556.71 kg/ha) than in the outer zone (558.25 kg/ha). Finally, yam yields are only recorded for the outer zone (125.82 kg/ha), possibly due to pesticide presence in the inner zones, which reduces soil fertility [35]. SO_2 and $Ca(OH)_2$ treatments appear to have improved soil reactivity and nutrient availability, which may explain the higher productivity in the outer zones, particularly for crops like cassava.

Table 6. Effects of cultivation zones on crop yield.

Crop	Zone	Yield (kg)	Yield per Hectare (kg/ha)	pH Change
Cassava	Inner	4377	875.4	Increase
Cassava	Outer	5879	979.8	Increase
Tomato	Inner	3897	556.7	Increase
Tomato	Outer	2233	558.3	Increase
Yam	Inner	-	-	Increase
Yam	Outer	1384	125.8	Increase

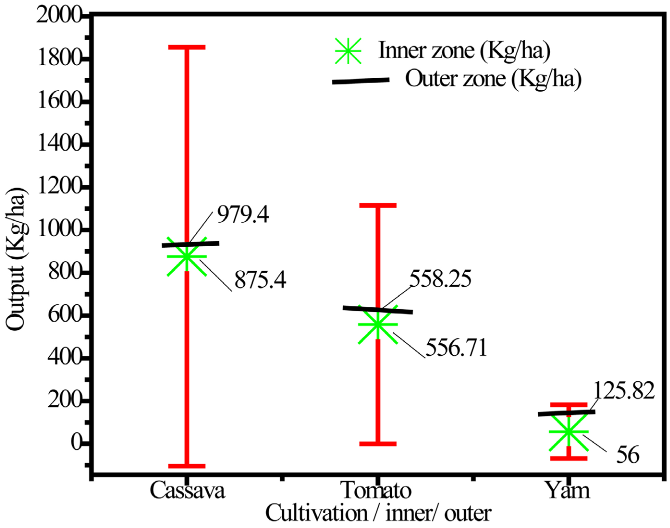


Figure 5. Comparison of crop yields in inner and outer zones with SO_2 and $Ca(OH)_2$ treatments.

3.9. FTIR Spectra of Untreated Soil before and after 180 Minutes of Grinding

Fourier transformed infrared technique was also applied to compare their difference of raw material (sample A) and the milled sample at 180 min as shown in Figure 6. The FTIR spectra of the untreated soil sample (before grinding), Figure 6(a) show several characteristic bands as 3347 cm^{-1}: Stretching of hydroxyl groups (−OH), likely associated with adsorbed water on the mineral surface and 1626 cm^{-1}: Bending of adsorbed water (H–O–H), similar to the 1642 cm^{-1} band in the reference extract and 1024 cm^{-1}: Si–O stretching, representing vibrations in the Si–O bonds of silicate minerals and 576 cm^{-1} [36], Si–O–Si bending, possibly linked to network deformation and 469 cm^{-1}: Si–O–Si bending, associated with deformation of the SiO_4 framework, consistent with the 468 cm^{-1} band in the reference [37]. After 180 minutes of grinding (**Figure 6(b)**), the 3347 cm^{-1} band shifts to 3456 cm^{-1}, indicating a change in hydration state. This shift suggests that grinding affects the surface sites, potentially redistributing adsorbed water or altering the coordination of hydroxyl groups. The 1024 cm^{-1} band before grinding and the 1030 cm^{-1}/1032 cm^{-1} bands after grinding remain relatively stable, implying that the fundamental structure of the mineral is not significantly altered by grinding [38]. The characteristic Si–O vibrations, such as Si–O stretching and Si–O–Si bending, show only slight shifts, indicating that the overall network remains stable [39]. The new band at 913 cm^{-1} after grinding suggests a modification of the hydration state, supporting earlier observations regarding the impact of grinding on deformation of the Al–OH bonds and adsorbed water [40]. Additionally, the absorption bands at 538 cm^{-1} and 470 cm^{-1} are attributed to the bending vibrations of Si–O–AlVI and Si–O–Si bonds respectively [40]-[42] showing small variations, though these changes are not significant in terms of structural modification.

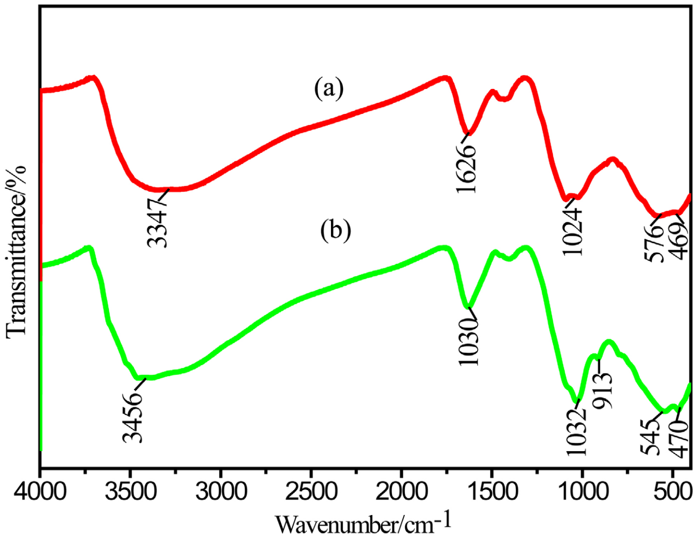


Figure 6. FTIR spectra showing the characteristic bands of the untreated soil sample before and after 180 minutes of grinding, in the range 3000 - 4000 cm^{-1} and 400 - 1030 cm^{-1}.

This study investigates the effects of chemical treatments and grinding on the reactivity and nutrient availability of halloysite-rich soils from the Djando Plateau, Moheli, Comoros. Halloysite, a clay mineral with high cation exchange capacity, is highly susceptible to pesticide contamination, which can negatively affect soil fertility. In this study, sulfur dioxide (SO_2) and calcium hydroxide $Ca(OH)_2$ were used as soil amendments to enhance potassium (K) extraction, modify soil pH, and alter the mineral structure. The findings show that both SO_2 and $Ca(OH)_2$ significantly improve potassium extraction, with $Ca(OH)_2$ yielding the highest potassium release (up to 70%) after 180 minutes of grinding. X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) analyses indicate that grinding disrupts the halloysite mineral structure, leading to increased surface area and enhanced reactivity. The addition of $Ca(OH)_2$ notably increases soil pH, neutralizing acidity and promoting nutrient availability, thus improving soil fertility. These chemical treatments improve potassium solubility and can help address nutrient deficiencies in soils impacted by pesticide use. The study further reveals that modifications to the soil structure, such as grinding and chemical treatment, can improve nutrient availability, promoting long-term agricultural sustainability. The findings highlight the importance of soil amendments like $Ca(OH)_2$ and SO_2 for enhancing soil fertility in regions affected by pesticide use and emphasize their potential in improving crop yields and soil health.

4. Conclusions

This study highlights the significant impact of chemical treatments, particularly SO_2 and $Ca(OH)_2$, on the mineralogical and chemical properties of halloysite-rich soils from the Djando Plateau, Mohéli, Comoros, after 20 years of pesticide exposure. The results demonstrate that these amendments enhance soil reactivity and potassium extraction, key factors for plant nutrition. Specifically, $Ca(OH)_2$ treatment achieved the highest potassium release efficiency (70%) after 180 minutes of grinding, while also raising soil pH to 7.6, indicating its strong alkalinizing effect. SO_2 treatment, though less pronounced, also contributed to improved potassium solubilization. X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy analyses confirmed substantial alterations in mineral structure, increasing chemical reactivity and surface area.

Despite these promising findings, the study has limitations that must be considered. The observed changes in potassium availability, pH, and mineral structure suggest potential benefits for soil fertility, but further long-term field studies are needed to confirm their effects on crop productivity and microbial activity. Additionally, the sustainability of these amendments, particularly in the context of repeated applications and potential secondary soil alterations, requires further investigation. These results underscore the importance of carefully evaluating soil treatments to optimize nutrient availability while ensuring long-term soil health in regions affected by intensive agricultural practices and pesticide contamination.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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