

# Effects of bentonite and zeolite minerals on mobility of lead in paddy soil in Chi Dao commune, Van Lam district, Hung Yen province, Vietnam

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Received 25 October 2021; revised 15 November 2021; accepted 28 November 2021

## Abstract:

Used lead-acid battery recycling activities in Minh Khai handicraft village, Chi Dao commune, Van Lam district, Hung Yen province, Vietnam has markedly increased the lead (Pb) content in paddy soil. Reducing the mobility of lead and lead accumulation in rice plants/plain rice are major priorities to reduce the impacts of lead in paddy soil. Application of the minerals zeolite (4A and Faujasite) and bentonite (natural and modified) to lead-contaminated soil has been carried out in lab scale for three years. The results showed the efficiencies in reducing accumulated lead in rice were 58 and 56% after adding the artificial additives zeolite 4A and zeolite Faujasite, respectively. These results were better than those of modified bentonite and natural bentonite, which were only 44 and 24%, respectively. The control efficiency of Pb accumulated in rice plants between the supplemented samples of zeolite Faujasite, zeolite 4A, modified bentonite, and natural bentonite were 69, 56, 42, and 40%, respectively, compared with the control samples. The addition of minerals to the soils has also resulted in decreases of the growth and yield of the experimental rice plants compared with the control samples. In this research, 0.1 to 0.2% of zeolite Faujasite showed the best results in terms of reducing Pb content in soil as well as low effect on plant growth. This research opens up on-site pollution control solutions for lead-contaminated agricultural soils.

**Keywords:** heavy metals, lead immobilizing, minerals, rice uptake.

**Classification number:** 5.3

## 1. Introduction

Lead content in natural soil ranges from 10 to 50 ppm [1]. Due to biogeochemical cycling changes and imbalances from manmade activities such as use of fertilizer [2, 3], manure [4], sludge disposals [5], or polluted irrigation water [6, 7] result in the accumulation of lead in soil and create risks to human health and ecology [8]. Lead in soil may be in a soluble form, or found as lead inorganic compounds  $PbS$ ,  $PbSO_4$ ,  $PbSO_4 \cdot PbO$ ,  $\alpha$ - $PbO$  [9], or be associated with organic compounds such as amino acids, fulvic acids, and humic acids [10]. The mobility of lead in soil is largely controlled by pH [11, 12], the presence of organic matter [13], and clay mineral content [14]. Lead phytoavailability and toxicity are dependent on their speciation.

Zeolite is the general name for aluminosilicate minerals called tectosilicates, which have three-dimensional frameworks [15]. Zeolite has high cation exchange capacity and selective absorption, so it is widely used in environmental treatment especially for heavy metal absorption in contaminated soils [16-19]. Chemical stabilization of heavy metals by adding artificial additives has been evaluated as one of the most cost effective in situ remediation techniques for metal contaminated sites [16, 20]. Chemical stabilization may lead to a decrease in extractable metal content in soil [21] and metal phytoavailability in plants [16, 22].

Used lead-acid battery recycling activities in Minh Khai handicraft village, Chi Dao commune, Van Lam district, Hung Yen province, Vietnam discharges copious amounts of acidic wastewater and causes soil and water pollution. Some studies reported that Pb concentration in soils in the handicraft village exceeded the allowable value [23, 24] and causes major health issues in the local community [25, 26]. Therefore the agricultural soil surrounding the handicraft village is not safe enough for cultivation.

This study was implemented to evaluate and determine a suitable in situ remediation for Pb-contaminated sites by adding artificial minerals into soils to immobilize lead and decrease its phytoavailability in rice plants. Some effects of additives on the rice growth (such as plant height, number of panicles, length, and weight of plain rice) in this study were also determined.

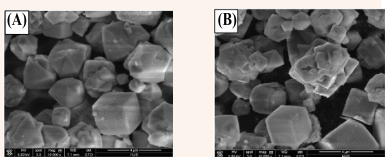
## 2. Materials and methods

### 2.1. Materials

**Zeolite minerals:** In this study, minerals of zeolite 4A and zeolite Faujasite were synthesized from silica particles of rice straw. The hydrothermal crystallization method was used to synthesize zeolite minerals and the products, shown in Table 1, were characterized using x-ray powder diffraction (XRD) and observed by scanning electron microscope (SEM).

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**Table 1. Properties of zeolite minerals.**

| No. | Element                                                   | Zeolite 4A                                                                           | Zeolite Faujasite                                                          |
|-----|-----------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| 1   | Chemical formula                                          | $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$ | $\text{Na}_2\text{Al}_2\text{Si}_{25}\text{O}_9 \cdot 6\text{H}_2\text{O}$ |
| 2   | Mineral compositions                                      | $\text{Na}_2\text{O}$ ; $\text{Al}_2\text{O}_3$ ; $\text{SiO}_2$                     | $\text{Na}_2\text{O}$ ; $\text{Al}_2\text{O}_3$ ; $\text{SiO}_2$           |
| 3   | Crystalline size, $\mu\text{m}$                           | 2.5                                                                                  | 4                                                                          |
| 4   | CEC, meq $100\text{ g}^{-1}$                              | 341                                                                                  | 432                                                                        |
| 5   | Pb absorption efficiency, %                               | 82.67                                                                                | 96.56                                                                      |
| 6   | SEM captured off (A) zeolite 4A and (B) zeolite Faujasite |     |                                                                            |

**Natural bentonite and modified bentonite minerals:** The natural bentonite in this research was collected from the Tam Bo bentonite mines, Di Linh district, Lam Dong province, Vietnam. The mineral was compounded by high Montmorillonite content (about 64%) while the remains were Kaolinite (9.5%), Illite (6.0%), Quartz (5.0%), Feldspar (3.5%), Goethite (3.0%), Canxit (little), and other minerals. Chemical compositions of the natural bentonite were mainly composed of  $\text{SiO}_2$  (50.5%),  $\text{Al}_2\text{O}_3$  (17.67%), and  $\text{Fe}_2\text{O}_3$  (7.0%). The mineral had a CEC of  $19.5\text{ meq } 100\text{ g}^{-1}$  and the basal spacing of  $15.49\text{ \AA}$ .

Al-pillared bentonite was created by activating the natural bentonite with polyoxymetal cations of Al solution. The activated mineral had CEC of  $58.6\text{ meq } 100\text{ g}^{-1}$  and the basal spacing of  $16.81\text{ \AA}$ .

**Contaminated-Pb soil samples:** Soil samples used in the research were collected from the 0-20 cm surface layers of 10 small scale paddy fields surrounding the used lead-acid battery recycling facilities in Minh Khai handicraft village, Chi Dao commune, Van Lam district, Hung Yen province, Vietnam (Fig. 1).

**Fig. 1. Soil sampling locations.**

**Rice plants:** Greenhouse pot experiments were conducted at the Vietnam National University of Agriculture (VNUA) and used to evaluate the effects of zeolite and bentonite minerals on the immobility of lead in soil and the growth and grain yield of rice plants. The Bac Thom No.7 resistance leaf blight variety was used in the pot experiments. Rice plants of age 10-13 days after sowing were planted in the experimental pots. Three rice plants with the same height were planted in each experimental pot.

**Rice grain samples:** The rice grains were used in this research to determine the effectivity of lead cumulative control after adding mineral additives to the soil. These rice grains were collected from the experimental pots.

## 2.2. Methods

**Soil analysis:** Soil samples were examined by the PIXE method (particle-induced x-ray emission) to determine its chemical composition. Other physio-chemical properties of the soil samples such as pH, electro-conductivity (EC), texture, and organic matter (OM) content were also determined.

**Plant-available Pb analysis:** Pb phytoavailability was extracted from soil by the diethylenetriamine pentaacetic acid (DTPA) method at a pH of 7.3. Each 10 g portion of air-dried soil was passed through a 2.0-mm sieve to which 20 ml DTPA extractant was added. The suspensions were shaken at 175 rpm for 2 h. The experiments were terminated by filtration of the suspension by a cellulose acetate filter, then determining the soluble ion of Pb using ICP-OES (PE 7300 V-ICP, Perkin Elmer).

**Determination of Pb content in rice plant and grain:** Pb content in rice plants and grains was determined by using aqua regia (3:1  $\text{HCl}/\text{HNO}_3$ ). Briefly, 50 mg of dried sample was drilled and digested in 50 ml of the aqua regia solution. The solution was then gently shaken and filtered by a cellulose acetate filter. The soluble ion of Pb was determined using ICP-OES (PE 7300 V-ICP, Perkin Elmer).

**Greenhouse pot experimental design method:** After assessing the composition and properties of the soil, the soil samples were mixed together and then NPK fertilizer was added with an amount of 25 kg per  $360\text{ m}^2$  (corresponding  $1.1\text{ g}$  per experimental pot). This soil was then filled into the experimental pots (30 cm diameter x 20 cm height). The experiment was conducted over three seasons. Four types of minerals (natural and modified bentonite, zeolite 4A, and zeolite Faujasite) with six treatments (5 levels of additives from 0.1 to 0.5% and the control) were replicated three times in one season resulting in 72 pots ( $4 \times 6 \times 3$ ) in total (Table 2). The weight of both soil and added mineral was 5 kg in total. The Bac Thom No.7 resistance leaf blight variety was used in the pot experiment, which was submerged in 5 cm of water over the entire growth period. Three seedlings 13 days in age

were planted in each pot. NPK 17-12-5 fertilizer with a dosage of 1.1 g per pot was supplemented three times during the experiment beginning at basal fertilizing (before experiment operation), then the first application of fertilizer (10 days after plantation), and second application addition fertilizer (49 days after plantation) (Table 3).

**Table 2. Lab-scale experimental design.**

| Element           | Control | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
|-------------------|---------|---------|---------|---------|---------|---------|
| Ration (w/w)      | 0%      | 0.1%    | 0.2%    | 0.3%    | 0.4%    | 0.5%    |
| Mineral amount, g | 0       | 5       | 10      | 15      | 20      | 25      |
| Soil amount, g    | 5,000   | 4,995   | 4,990   | 4,985   | 4,980   | 4,975   |
| Total, g          | 5,000   | 5,000   | 5,000   | 5,000   | 5,000   | 5,000   |

**Table 3. Growth stages of rice plant and evaluated elements.**

| No | Stages            | Time, day | Element                                                                                                                                                                             |
|----|-------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1  | Seeding           | 13        | Pb total, extractable Pb in soil, pH <sub>KCl</sub>                                                                                                                                 |
| 2  | Transplanting     | 26        | - Extractable Pb in soils<br>- pH <sub>KCl</sub>                                                                                                                                    |
| 3  | Tillering         | 36        |                                                                                                                                                                                     |
| 4  | Panicle formation | 49        |                                                                                                                                                                                     |
| 5  | Flowering         | 61        |                                                                                                                                                                                     |
| 6  | Harvest           | 109       | - pH <sub>KCl</sub> , extractable Pb in soil, Pb content in rice plant and polished rice, height of rice plant, number of panicles, length of rice grain and weight of 1000 grains. |

### 3. Results and discussion

#### 3.1. Compositions and properties of soil samples

The results show that soil pH<sub>KCl</sub> values ranged from 3.4 to 5.2 with an average of 4.1. The soil in the study area is acidic. Although the sampling locations were within a narrow area, the variations in pH<sub>KCl</sub> value were relatively large. This can be explained by external effects such as the use of wastewater containing high H<sup>+</sup> ions discharged from the village for irrigation. The low pH<sub>KCl</sub> values in soil may lead to increase in the risk of pollution by mobilizing heavy metals and thus increasing its bioavailability for plants [27] (Table 4).

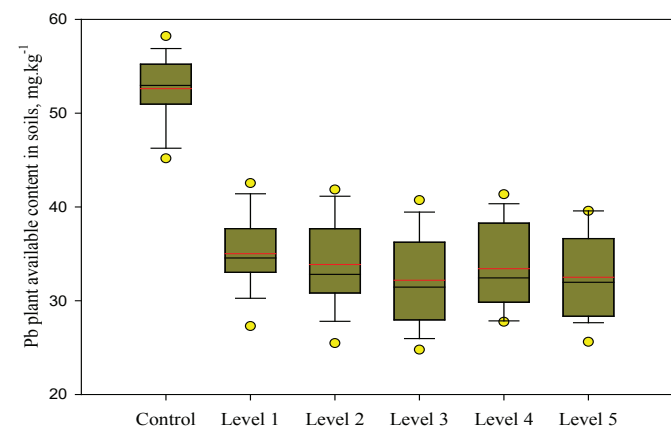
The OM contents of soil samples ranged from 1.33 to 2.44%. According to the Ministry of Natural Resources and Environment (2015) [28], the soil samples from this area were from the low-to-medium organic matter content groups (from 2.60-3.36%). Soil texture analysis showed that the proportion of clay ranged from 3.7 to 8.0%, limon from 50.0 to 63.1%, and sand from 32.1 to 46.3%. The average CEC value was about 12.8 meq 100g<sup>-1</sup>. These low CEC and organic matter values contribute to conditions that make the exchange of Pb content in the soil high. Total Pb content in the 10 soil samples ranged from 403.8 to 1766 mg kg<sup>-1</sup> with an average of 999±322.28 mg kg<sup>-1</sup>.

**Table 4. Soil compositions and properties in the study.**

| Parameters                 | Soil sample No.  |                  |                  |                  |                  |                  |                  |                  |                  |                 |
|----------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------|
|                            | S <sub>01</sub>  | S <sub>02</sub>  | S <sub>03</sub>  | S <sub>04</sub>  | S <sub>05</sub>  | S <sub>06</sub>  | S <sub>07</sub>  | S <sub>08</sub>  | S <sub>09</sub>  | S <sub>10</sub> |
| pH <sub>KCl</sub>          | 3.40<br>(±0.01)  | 3.59<br>(±0.01)  | 3.41<br>(±0.01)  | 3.90<br>(±0.01)  | 4.14<br>(±0.01)  | 3.92<br>(±0.01)  | 4.65<br>(±0.02)  | 4.59<br>(±0.01)  | 3.69<br>(±0.01)  | 5.20<br>(±0.03) |
| OM (%)                     | 2.44<br>(±0.02)  | 2.24<br>(±0.02)  | 2.39<br>(±0.05)  | 2.09<br>(±0.02)  | 1.89<br>(±0.02)  | 2.90<br>(±0.05)  | 2.04<br>(±0.02)  | 2.12<br>(±0.02)  | 2.60<br>(±0.05)  | 1.33<br>(±0.04) |
| EC (μS cm <sup>-1</sup> )  | 305.3<br>(±5.51) | 339.3<br>(±9.71) | 234.3<br>(±17.6) | 163.3<br>(±2.46) | 178.7<br>(±11.3) | 165.2<br>(±4.07) | 129.5<br>(±4.90) | 156.2<br>(±4.16) | 163.5<br>(±4.15) | 92.6<br>(±2.20) |
| CEC meq 100g <sup>-1</sup> | 13.0<br>(± 3.7)  | 15.4<br>(± 1.9)  | 12.2<br>(±4.6)   | 11.4<br>(± 3.1)  | 11.6<br>(± 4.7)  | 13.2<br>(± 1.5)  | 12.7<br>(±0.8)   | 11.9<br>(±3.4)   | 13.5<br>(± 2.4)  | 12.8<br>(± 4.6) |
| Pb, mg kg <sup>-1</sup>    | 1,116            | 921              | 1,014            | 1,090            | 1,766            | 972              | 816              | 827              | 1,064            | 404             |
| Cu, mg kg <sup>-1</sup>    | 218.3            | 208.3            | 184.2            | 240.0            | 297.0            | 178.4            | 189.5            | 189.3            | 209.8            | 183.5           |
| Zn, mg kg <sup>-1</sup>    | 219.5            | 228.7            | 271.7            | 289.7            | 264.5            | 263.0            | 202.7            | 200.1            | 220.3            | 174.3           |
| Ni, mg kg <sup>-1</sup>    | 44.09            | 38.98            | 46.20            | 46.99            | 39.72            | 40.61            | 47.18            | 40.05            | 39.99            | 44.37           |

#### 3.2. Effects of minerals on plant-available Pb in soil and Pb-uptake by rice plant

*Effects on plant-available Pb content in soils:* Analysis results after three consecutive experiments showed that there was a signification decrease in the concentration of Pb extracted by the DTPA solution when the four types of adsorbents at different levels were added. The average mobile Pb content in the control sample was 53.94 mg kg<sup>-1</sup>. After the experiment (over 3 crops, 109 days for summer-autumn crop or 137 days for winter-spring crop), the average content over 3 crops of mobile Pb was about 32.26 mg kg<sup>-1</sup> achieving an efficiency of about 40.14% reduction in soluble Pb content in the soil (Fig. 2). One-way ANOVA analysis showed that the difference in Pb content values between the control and mineral added samples was significant (p<0.05).



**Fig. 2. Plant-available Pb content in soils in relation to minerals added.** Amount of added minerals, level 1: 0.1%; level 2: 0.2%, level 3: 0.3%, level 4: 0.4%; level 5: 0.5%. The above Pb contents were calculated by the average value of 4 minerals within 3 crops.



Although the immobility of Pb in soil by two minerals of zeolite and bentonite was relatively good during the whole experiment, there was a significant difference between the growth stages of the rice plants. The effect of minerals on Pb mobility was shown immediately after two growth stages of sowing (day 13) and transplanting (day 26). In the subsequent stages, the degree of reduction in mobile Pb content was lower. The impact of minerals reached an equilibrium state after the first two growth stages of the rice plants (Fig. 3).

**Effects on Pb content uptake by rice plant:** The results from three experimental crops showed a significant difference in Pb content in rice plants depending on the type and level of minerals added to the soil. All of the mineral-supplemented pots showed a lower Pb accumulated content in rice compared to the control pots. The ability of the minerals to control Pb accumulation in rice plants ranged from 24 to 58% compared to the control samples. The efficiency of reducing Pb accumulation in rice plants treated with the minerals zeolite 4A and zeolite Faujasite was 58 and 56%, respectively, which was better than the modified and natural bentonite minerals (44 and 24%,

respectively). The largest content of Pb intake in the rice plants reached  $78.76 \text{ mg kg}^{-1}$  (dry biomass) at the pot with natural bentonite added, meanwhile, the lowest Pb content was only  $52.41 \text{ mg kg}^{-1}$  with the supplementation of zeolite 4A. In the two experiments that added zeolite Faujasite and modified bentonite, the amount of Pb accumulated in rice was  $57.07 \text{ mg kg}^{-1}$  and  $70.82 \text{ mg kg}^{-1}$ , respectively (Fig. 4).

There is a relatively strong correlation between the Pb content accumulation in rice plants and the additional mineral levels as seen from  $R^2$  ranging from 0.66 to 0.94 ( $n=15$ ). Although the capacity to control Pb content in rice varied between the types of mineral supplementation, the general trend for all four materials was that Pb concentration in rice decreased with the increase of mineral amount added to the soil.

**Effects on Pb contents in rice grain:** There was a significant difference in the extracted Pb content between the control and mineral-added samples for all four types of adsorbent. The general trend was that the Pb content of rice was much lower than that of the control treatment. The more mineral

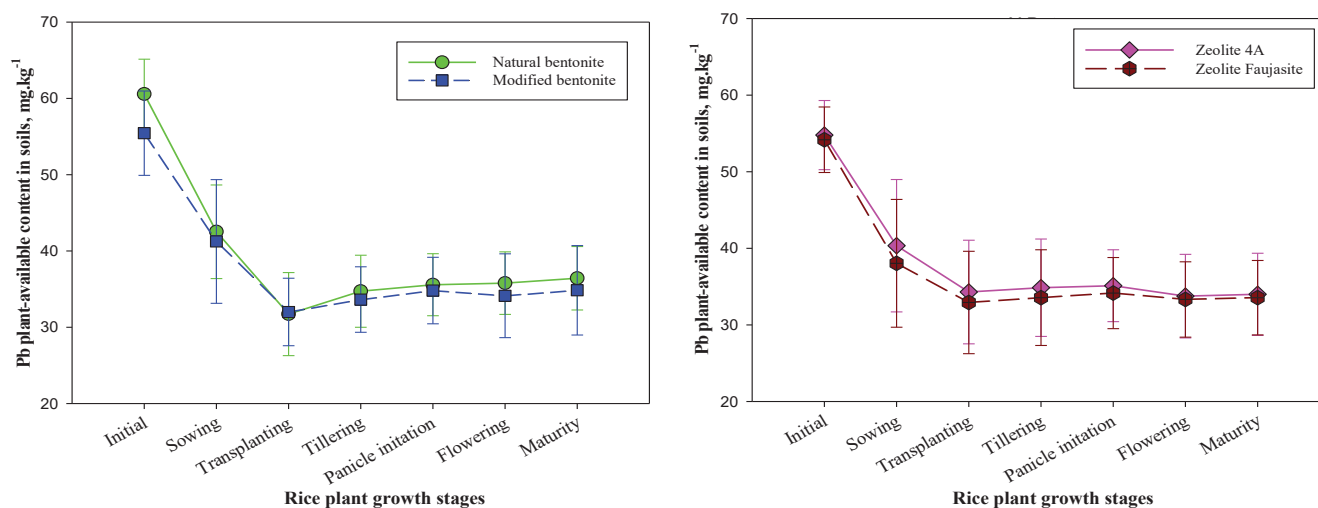


Fig. 3. Ranges of soluble Pb content in soil during growth stages of rice plants.

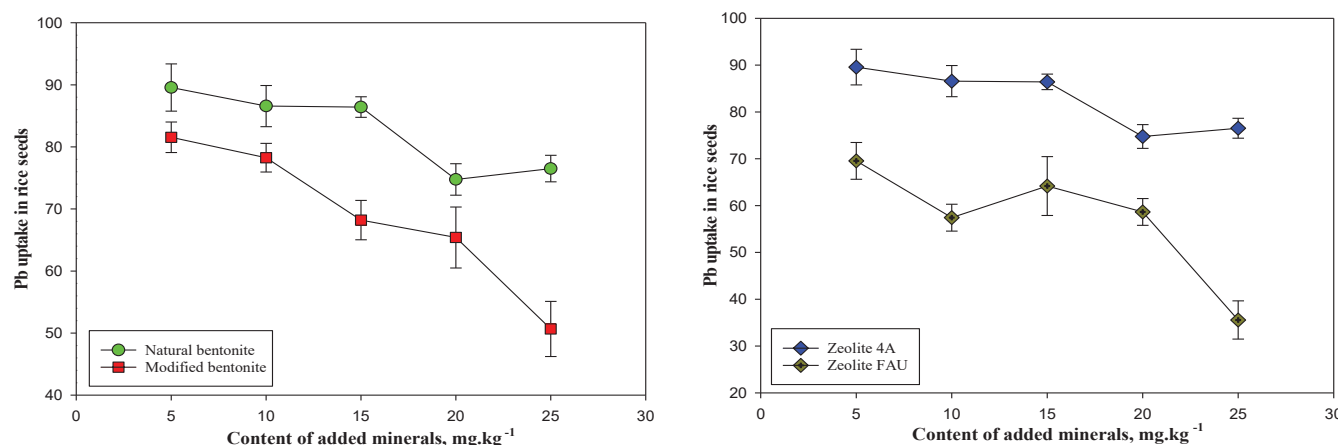


Fig. 4. Pb content accumulated in rice plants with amount of added minerals.

supplementation, the lower the Pb content in rice. The mean impact of controlling Pb content in rice when comparing the supplement levels of zeolite Faujasite, zeolite 4A, modified bentonite, and natural bentonite was 69, 56, 42, and 40%, respectively (Table 5).

**Table 5. Intake Pb contents in rice grain.**

| Type of minerals            | Pb contents in rice grain, ( $\mu\text{g}\cdot\text{g}^{-1}$ ) |               |               |               |               |               |
|-----------------------------|----------------------------------------------------------------|---------------|---------------|---------------|---------------|---------------|
|                             | Control                                                        | Level 1       | Level 2       | Level 3       | Level 4       | Level 5       |
| Natural bentonite           | $0.81\pm0.01$                                                  | $0.42\pm0.02$ | $0.57\pm0.06$ | $0.65\pm0.05$ | $0.39\pm0.03$ | $0.42\pm0.04$ |
| Modified bentonite          | $0.78\pm0.05$                                                  | $0.40\pm0.03$ | $0.54\pm0.11$ | $0.56\pm0.09$ | $0.38\pm0.06$ | $0.38\pm0.03$ |
| Zeolite 4A                  | $0.75\pm0.07$                                                  | $0.58\pm0.06$ | $0.37\pm0.09$ | $0.26\pm0.08$ | $0.20\pm0.01$ | $0.24\pm0.02$ |
| Zeolite Faujasite           | $0.67\pm0.05$                                                  | $0.35\pm0.16$ | $0.23\pm0.04$ | $0.23\pm0.06$ | $0.12\pm0.03$ | $0.11\pm0.03$ |
| Std. threshold <sup>†</sup> | $0.2\ \mu\text{g}\cdot\text{g}^{-1}$                           |               |               |               |               |               |

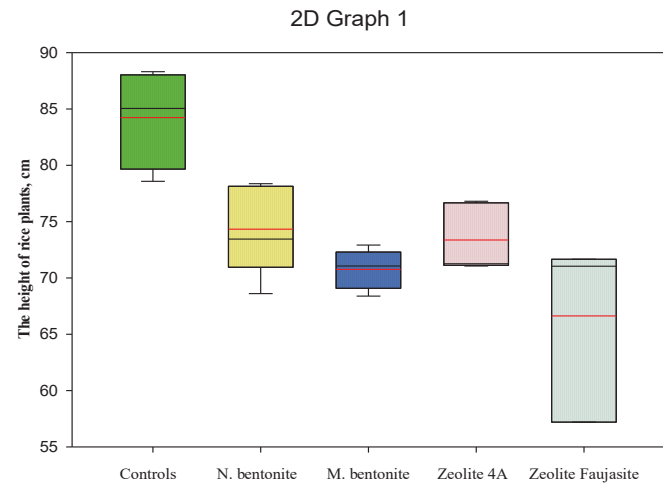
Amount of added minerals, level 1: 0.1%; level 2: 0.2%, level 3: 0.3%, level 4: 0.4%; level 5: 0.5%; <sup>†</sup>: QCVN 8-2:2011 of the Ministry of Health.

The content of Pb accumulated in rice varied considerably ( $0.11$  to  $0.65\ \mu\text{g}\cdot\text{g}^{-1}$ ) between mineral added levels, and these values were lower than that of the control samples (from  $0.67$  to  $0.81\ \mu\text{g}\cdot\text{g}^{-1}$ ). The mean Pb intake by rice among the mineral supplements was significantly different when compared with the control sample ( $p<0.05$ ,  $n=9$ ). The most general trend was that Pb intake in rice decreased in accordance with an increase in added mineral amount. Artificial minerals of the zeolite group have better control on Pb accumulation in rice than minerals of the bentonite group. The content of Pb in different parts of the plant tended to decrease in the order of root > stem > leaf > flower > seed. J. Liu, et al. (2003) [29] showed that the ratio of Pb content in root:stem:leaf of the rice plants was 60:5:1 at the flowering stage and 19.4:2.9:1 at the mature stage. In this study, Pb concentrations in rice plants were 155 to 274 times greater than that in polished rice. This is because the fixation of Pb to the root cell wall is greater than that of other plant parts [30]. The addition of minerals to the soil reduced the Pb accumulation in rice plants and this led to a decrease in the accumulation of Pb in rice grains. Due to the higher CEC of the artificial minerals in the zeolite group (zeolite 4A and Faujasite zeolite are 341 and 432 meq.100  $\text{g}^{-1}$ , respectively) compared to the bentonite group (natural bentonite and modified bentonite are 19.5 and 58.6 meq.100  $\text{g}^{-1}$ , respectively), a difference in the Pb concentration in the rice grain is understood.

### 3.3. Effects of minerals on rice plant grow

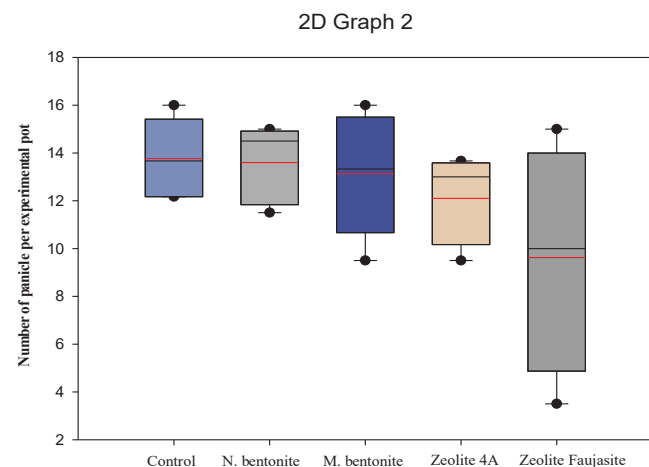
**Effects on rice plant's height:** At the mature stage, the height of the rice plants in all experimental treatments reached an average value of 67.65 cm. However, the growth heights of these plants varied between different types of added minerals. While the average height of the rice plants in the control sample was 84.25 cm, the maximum growth height in the formula with natural bentonite was only 74.33 cm.

The lowest height occurred with the Faujasite zeolite mineral supplement experiment at only 66.64 cm. The average heights of the rice plants in the two treatments supplemented with zeolite 4A and modified bentonite was 73.38 cm and 70.77 cm, respectively (Fig. 5). The research by N. Hung, et al. (2019) [31] showed that less than 10  $\text{mg}\cdot\text{kg}^{-1}$  Pb content in soil can promote rice growth and increase tillering ability and root length. However, concentrations greater than 10  $\text{mg}\cdot\text{kg}^{-1}$  will inhibit the tillering stage and plant height ( $R^2=0.8-0.9$ ,  $p<0.05$ ).



**Fig. 5. The height of rice plants in different rate of added minerals.**

**Effects on the number of rice panicle:** The average number of rice panicles obtained in the experiments of adding natural bentonite, modified bentonite, and zeolite 4A was 11.2, 12.4, and 12.8 panicles per crop, respectively. For zeolite Faujasite, the average number of panicles was only 9.0 per crop. Thus, the rice cultivation efficiency of the soil amended with Faujasite zeolite was much lower than that of other minerals. In addition, the average number of rice panicles of the experimental treatments was also 14.17 panicles lower than that of the control samples. These results show that the amount of rice panicles



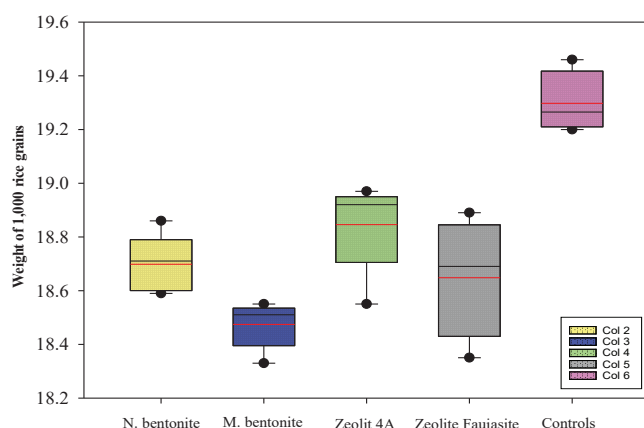
**Fig. 6. Number of rice panicles based on the type of mineral added.**

was significantly affected by the amount of minerals added to the cultivated soil environment, especially for Faujasite zeolite at the levels of 0.4-0.5% by weight (Fig. 6).

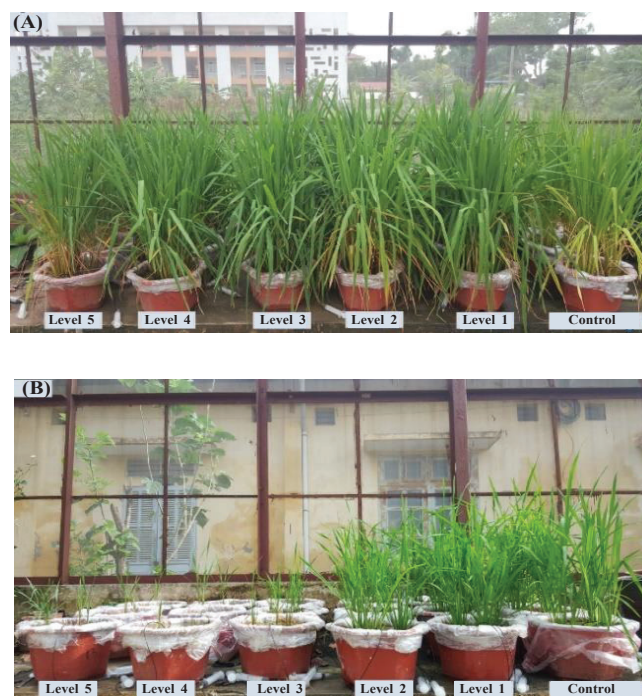
**Effects on the length and weight of rice grain:** The obtained average rice grain length ranged from 5.88 to 6.25 mm, meanwhile, this value in the control sample was 6.27 mm. With the average grain length of the blight-resistant Bac Thom No. 7 cultivated under the standard conditions of 6.2 - 6.3 mm, all four experiments in this study yielded lower mean grain lengths than those in the control sample (Table 6). The weight of 1,000 grains of rice listed from 4 experimental formulas in this study ranged from 18.47 to 18.85 grams/1,000 seeds (Fig. 7). Both agronomic indicators of rice yield (the length and weight of 1,000 grains) showed that these values in the mineral-added formulas were lower than in the control ( $p < 0.05$ ,  $n = 12$ ) and lower than in the normal growth conditions of the rice varieties, which are 6.2-6.3 cm and 19.0, respectively [32].

**Table 6. The length and weight of 1000 rice grains ( $n = 3$ ).**

| Additives          | Parameters                | Control    | Level 1    | Level 2    | Level 3    | Level 4    | Level 5    |
|--------------------|---------------------------|------------|------------|------------|------------|------------|------------|
| Natural bentonite  | Length of seed (mm)       | 6.29±0.01  | 6.14±0.02  | 6.13±0.01  | 6.18±0.05  | 6.01±0.13  | 6.25±0.04  |
|                    | Weight of 1000 grains (g) | 19.46±0.05 | 18.61±0.28 | 18.86±0.13 | 18.72±0.16 | 18.59±0.10 | 18.71±0.21 |
| Modified bentonite | Length of seed (mm)       | 6.22±0.04  | 6.11±0.09  | 6.07±0.15  | 5.88±0.15  | 6.02±0.17  | 5.88±0.18  |
|                    | Weight of 1000 grains (g) | 19.20±0.22 | 18.55±0.26 | 18.52±0.12 | 18.46±0.04 | 18.33±0.26 | 18.51±0.19 |
| Zeolite 4A         | Length of seed (mm)       | 6.30±0.02  | 6.23±0.05  | 6.17±0.13  | 6.16±0.08  | 6.09±0.18  | 6.01±0.21  |
|                    | Weight of 1000 grains (g) | 19.29±0.34 | 18.92±0.28 | 18.93±0.18 | 18.97±0.17 | 18.86±0.06 | 18.55±0.21 |
| Zeolite Faujasite  | Length of seed (mm)       | 6.26±0.03  | 5.99±0.15  | 5.99±0.10  | 6.21±0.04  | 6.01±0.04  | 6.25±0.02  |
|                    | Weight of 1000 grains (g) | 19.24±0.20 | 18.51±0.09 | 18.89±0.10 | 18.80±0.28 | 18.35±0.24 | 18.69±0.35 |



**Fig. 7. Weight of 1,000 rice grains under different amount of added minerals.**



**Fig. 8. (A) The relatively uniform growth and (B) the phenomenon of dead of plants with the addition of zeolite Faujasite in the first crop.**

The decline in the growth and yield of rice plants can be explained by the fact that materials with a very high cation-exchange capacity (CEC) have claim on the nutrient minerals in the soil and reduce the plant's access to these nutrients thus affecting some agricultural agronomic indicators of the rice plants.

#### 4. Conclusions

The agricultural soil for rice cultivation in Minh Khai village, Chi Dao commune, Van Lam district, Hung Yen province is acidic ( $pH_{KCl}$  ranges from 3.4 to 5.2), has low cation exchange capacity (about  $13.2 \text{ meq.}100 \text{ g}^{-1}$ ), and is classified from silty to sandy silt. Pb content in soil in the area surrounding the craft village is at a high level, which is 17 times higher than the National Technical Regulation on the allowable limits of heavy metals in soils. The addition of minerals of zeolite and bentonite groups at the rate of 0.1 to 0.5% significantly reduced the mobility of Pb metal in the soil solution extracted by DTPA. The efficiency of reducing the mobile Pb content in soil decreased from 24 to 58% compared with the control sample. The ability to control Pb flexibility in the soil of the zeolite mineral group was higher than that of the bentonite group. The effect of reducing the flexible Pb content in the soil led to a decrease in Pb accumulation in rice and rice plants ( $R^2 = 0.66-0.93$ ;  $n = 15$ ). The addition of minerals of the zeolite and bentonite groups had a deterrent effect on the growth and yield of experimental rice plants. The most appropriate mineral



supplementation ratio in this study was found to be between 0.1 and 0.2%. From the research results, it is possible to use artificial zeolite minerals from agricultural by-products or modified bentonite minerals to limit the mobility of  $Pb^{2+}$  metal in the soil and reduce its accumulation in plants.

### CRediT author statement

Tu Ngoc Nguyen, Huy Quang Trinh, Cong Huu Vo: Data curation, Software, Visualisation, Investigation, Writing, Methodology, Supervision, Revising the manuscript.

### COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article

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