Desalination and Water Treatment 319 (2024) 100489

Contents lists available at ScienceDirect

Desalination and Water Treatment

journal homepage: www.sciencedirect.com/journal/desalination-and-water-treatment/

# Mitigating water pollution by nitrogen fertilizers through amending ammonium sorption in an acid soil using Calciprill and sodium silicate

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## ARTICLE INFO

*Keywords:*
Adsorption
Calcium carbonate
Desorption
Freundlich isotherm
Langmuir isotherm
*Piper nigrum*
Silicon
Water quality

## ABSTRACT

Use of nitrogen (N) fertilizers is gaining popularity to meet crop nutrient requirement for sustaining the food security of the increasing global population. However, improper management of N fertilizers in acid soils causes leaching and surface runoff because of excessive rainfalls and poor N retention in the tropics in particular. This results in N pollution in water bodies (also known as eutrophication), which degrades water quality to the detriment of aquatic ecosystems near farms. Thus, there is a need for using inorganic soil amendments such as Calciprill and sodium silicate to improve soil N adsorption because of the alkalinity and ability of these amendments to retain N for mitigating excessive N contamination in water bodies. To this end, this N sorption study was conducted to determine the effects of Calciprill and sodium silicate on ammonium ($NH_4^+$) adsorption and desorption in an acid soil (Bekenu series, *Typic Paleudults*). The soil was co-applied with different rates of Calciprill (80 %, 90 %, and 100 % Ca saturations) and sodium silicate (90, 105, 120, 135, and 150 kg $ha^{-1}$), followed by the $NH_4^+$ adsorption capacity determination through the additions of $NH_4^+$ isonormal solutions at the five concentrations (0, 25, 50, 75, and 100 mg $L^{-1}$) to establish a linear relationship between the amount of $NH_4^+$ absorbed ($q_e$) and the amount of $NH_4^+$ left in the solution ($C_e$) after 24 h of equilibration. Apart from the soil only without any amendment (C0S0), there were another two additional treatments where the soil was added with Calciprill (100 % Ca saturation) (C3) and sodium silicate only (150 kg $ha^{-1}$) (S5) to determine their respectively effects on N sorption. The collected data were fitted to the Langmuir and Freundlich isotherms. Thereafter, $NH_4^+$ desorption was determined using the same soil samples added with 2 mol $dm^{-3}$. Compared with the soil without any amendment (C0S0), the Calcirpill alone (C3) and the combined use of Calciprill and sodium silicate significantly increased $NH_4^+$ adsorption at the $NH_4^+$ addition of 250 mg $L^{1}$, suggesting that Calciprill is the amendment which dominantly increases $NH_4^+$ adsorption and the effects of amendments are more pronounced at the lower soil $NH_4^+$ concentration. The results also revealed that the $NH_4^+$ adsorption in the soils following the co-application of Calciprill and sodium silicate followed the assumption of Freundlich isotherm. Regardless of the $NH_4^+$ concentration used, the effects of Calciprill and sodium silicate on the $NH_4^+$ desorption remain unclear, which could be because of the ability of sodium silicate to stabilize the soil structure. This stabilization reaction might have impeded the dissolution of Calciprill and temporarily fixed the absorbed $NH_4^{+\cdot}$ These findings suggest that it is possible to use the amendments to amend $NH_4^+$ sorption in Bekenu series for mitigating $NH_4^+$ leaching and runoff to prevent eutrophication.

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https://doi.org/10.1016/j.dwt.2024.100489
Received 26 September 2023; Accepted 14 March 2024

## 1. Introduction

In the tropics, high rainfall and warm temperatures accelerate weathering to form infertile soils which are characterized by low pH, low organic matter content, low nutrient holding capacity, and low pH buffering capacity, resulting in considerable leaching of essential plant nutrients, for example $NH_4^+$ and $NO_3^-$ [21,24,55]. The rapid changes in soil chemical properties can significantly influence the availability of $NH_4^+$ and $NO_3^-$ for crop uptake. For example, in these highly weathered soils (pH < 5), high concentrations of hydrogen ($H^+$), aluminium ($Al^{3+}$), and iron ($Fe^{3+}$) ions can outcompete the $NH_4^+$ from being adsorbed at the limited negatively charged exchangeable sites of kaolinite clay minerals [16,56]. The free moving $NH_4^+$ in the soil solution could rapidly transform into $NO_3^-$ through nitrification, after which these mobile $NO_3^-$ are leached into surface and groundwater bodies because of the columbic repulsive forces by the soil negatively-charged sites to repel $NO_3^-$ [14,67]. To maintain the desirable soil and crop productivity, extensive N fertilizer application was adopted by the farmers to saturate the soils with plant available N. However, this approach is not sustainable because it is expensive and environmental unfriendly [18]. For example, according to Sulok et al. [59], the costs of chemical fertilizers used for one hectare of immature and mature black pepper vines are USD 1670 and USD 2131 per annual, respectively. The excessive and continuous application of N fertilizers without a proper management also causes N leaching which leads to environmental problems such as eutrophication at the adjacent streams to the farms and soil acidification ([43,64]). According to Sun et al. [60], approximately 24.75 % of N fertilizers applied were lost to the environment via ammonia volatilization, surface runoff, and leaching.

To overcome the aforementioned challenges, it is essential to understand that the N availability in the soil solution for crop absorption is reflected by sorption processes called adsorption and desorption. Adsorption is a process where nutrients are removed from the soil solution and attached onto the binding sites or surfaces of soil colloids, whereas desorption is the reverse of adsorption where the captured nutrients are released from the soil binding sites into the soil solution for crop uptake [23]. The N adsorption and desorption in soils vary with nutrient dynamics pathways [16], type of amendments added [43,49], soil pH [13,50,68], pH buffering capacity [45], soil mineralogy and amount of clay [41,63], organic matter [17,23,30], and cation exchange capacity (CEC) [54].

Therefore, the adsorption and desorption of nutrients can be amended by fixing the problems of these problematic soils through using liming amendments to increase soil pH, pH buffering capacity, and number of negatively charged exchangeable sites to temporarily retain the $NH_4^+$ for optimum crop uptake. Latifah et al. [22] opined that clinoptilolite zeolite is an effective absorbent which is capable of enhancing $NH_4^+$ and $NO_3^-$ retention released from the urea because of its alkalinity to increase pH and high CEC to improve adsorption capacity of acid soil (Bekenu series, *Typic Paleudults*). Fidel et al. [13] reported that the optimum soil pH range for maximizing $NH_4^+$ adsorption is 7 to 7.5 because of the maximum number of negative charged exchangeable sites to adsorb more $NH_4^+$ from the soil solution. In a 30-day leaching experiment, Ng et al. [39] demonstrated that co-application of Calciprill and sodium silicate reduces the leaching of $NO_3^-$ by 74.8 % because sodium silicate is reputed for reducing soil permeability in addition to increasing pH for suppressing nitrification. Ng et al. [40] also demonstrated that combined use of Calciprill and sodium silicate significantly improves $NH_4^+$ and reduces $NO_3^-$ availability because of the improved soil pH and effective CEC reduce nitrification. Furthermore, the calcium carbonate ($CaCO_3$) and sodium silicate were co-applied to extend the shelf life of ammonium nitrate fertilizer from degradation and caking through formation of stabilized crystal structure on the surface of fertilizer [15].

Based on the aforementioned rationale, the combined use of Calciprill and sodium silicate is a soil management approach which is worthy of consideration to improve $NH_4^+$ sorption in the highly weathered acidic soils. Calciprill has an advantage over the conventional liming materials such as ground magnesium limestone (GML), calcium carbonate powder, and dolomite because of its higher $CaCO_3$ purity (95 %) and neutralizing value (99) to increase soil pH and mitigate exchangeable acidity rapidly. The dissolution of Calciprill could release calcium ($Ca^{2+}$) and carbonate ($CO_3^{2-}$) ions where $Ca^{2+}$ could increase soil base saturation, impair Al and Fe hydrolysis, and suppress soil acidity, whereas $CO_3^{2-}$ could neutralize $H^+$ in the soil solution in addition to creating a new pool of negatively charged sites in the soil to improve the retention of $NH_4^+$ [1,23]. Sodium silicate is a silicon-based fertilizer which dissolves readily in soil water to release sodium ($Na^+$) and silicate ($SiO_3^{2-}$) ions, which improves soil pH [2,53], stabilize soil structure through the formation of silica gel between soil pores [27], increase soil water holding capacity [52], and improve nutrient retention because of presence of $SiO_3^{2-}$ [10,39,47].

To date, there is a dearth of information on the combined use of Calciprill and sodium silicate on $NH_4^+$ sorption of Bekenu series (*Typic Paleudults*). It is hypothesized that the co-application of Calciprill and sodium silicate could improve $NH_4^+$ adsorption to prevent N leaching and runoff which can result in eutrophication because the presence of $CO_3^{2-}$ and $SiO_3^{2-}$ could increase soil pH and number of negatively-charged sites. Therefore, this N sorption study was conducted to determine the effects of Calciprill and sodium silicate on $NH_4^+$ sorption of Bekenu series soil (*Typic Paleudults*). It is hoped that this study provide a deeper understanding about the mechanisms of improving $NH_4^+$ retention in the highly weathered acid soil amended with combined use of Calcirpill and sodium silicate to mitigate N pollution in surface and underground water bodies in addition to improving the fertilization regime of black pepper farming system.

## 2. Materials and methods

### 2.1. Soil sampling and amendment preparation

The acid soil used for this N sorption was Bekenu series (*Typic Paleudults*), based on USDA soil classification system. The soil was sampled in a pedon from (1 m length × 1 m width × 0.2 m depth) using hoe and shovel from an uncultivated area at Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia (03°20′N and longitude 113°07′E). Therefrom, the soil sample was air-dried, manually crushed, sieved to pass a 2 mm sieve, and bulked for homogenization. The Calciprill and sodium silicate were supplied by Omya Asia Pacific Sdn. Bhd., Kuala Lumpur, Malaysia and Humibox Sdn. Bhd., Kuala Lumpur, Malaysia, respectively.

### 2.2. Initial characterization of soil, Calciprill, and sodium silicate

Before commencing the N sorption, the bulked soil sample was analysed for its bulk density [61], texture [4], pH in water and electrical conductivity (EC) [44], exchangeable $NH_4^+$ and available $NO_3^-$ [20,5], exchangeable cations ($K^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $Fe^{2+}$, and $Mn^{2+}$) [32], exchangeable acidity and $Al^{3+}$ [51], cation exchange capacity (CEC) [11], and crude silica [65] using standard procedures, as summarized in Table 1. The similar standard procedures were used to determine the selected chemical properties of Calciprill and sodium silicate (pH in water, EC, exchangeable $NH_4^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $Fe^{2+}$, and $Mn^{2+}$, available $NO_3^-$, and crude silica), as presented in Table 2.

### 2.3. Surface morphology and elemental composition analysis for Calciprill and sodium silicate

Surface morphology of Calciprill and sodium silicate were determined using Scanning Electron Microscopy (SEM) (JEOL JSM-IT500 HR), whereas the elemental composition of the amendments was

**Table 1**
Selected physico-chemical properties of Bekenu series (*Typic Paleudult*) used in the ammonium sorption study.

| Soil physico-chemical properties | Value determined |
|---|---|
| Bulk density (g cm$^{-3}$) | 1.20 |
| Texture | Sand: 48.2 %; Silt: 24.2 %; Clay: 27.6 %∴ Loam Soil |
| pH$_{water}$ | 5.13 |
| Electrical Conductivity (µS cm$^{-1}$) | 8.87 |
| | (mg kg$^{-1}$) |
| Exchangeable NH$_4$$^+$ | 28.0 |
| Available NO$_3$$^-$ | 15.9 |
| Exchangeable K$^+$ | 76.0 |
| Exchangeable Ca$^{2+}$ | 17.1 |
| Exchangeable Mg$^{2+}$ | 20.4 |
| Exchangeable Na$^+$ | 7.8 |
| Exchangeable Fe$^{2+}$ | 476.9 |
| Exchangeable Mn$^{2+}$ | 6.1 |
| | (cmol$_{(+)}$ kg$^{-1}$) |
| Exchangeable acidity | 1.21 |
| Exchangeable Al$^{3+}$ | 1.03 |
| Cation Exchange Capacity | 7.70 |
| Crude silica (%) | 7.98 |

**Table 2**
Selected chemical properties of Calciprill and sodium silicate used in the ammonium sorption study.

| Chemical properties | Calciprill | Sodium silicate |
|---|---|---|
| pH$_{water}$ | 7.77 | 12.96 |
| Electrical conductivity (dS m$^{-1}$) | 3.11 | 113.17 |
| | (mg kg$^{-1}$) | |
| Exchangeable NH$_4$$^+$ | 7.47 | 8.41 |
| Available NO$_3$$^-$ | 8.41 | 12.14 |
| | (cmol$_{(+)}$ kg$^{-1}$) | |
| Exchangeable K$^+$ | 0.80 | 0.67 |
| Exchangeable Ca$^{2+}$ | 48.48 | trace |
| Exchangeable Mg$^{2+}$ | 0.87 | 0.02 |
| Exchangeable Na$^+$ | 16.55 | 876.07 |
| Exchangeable Fe$^{2+}$ | 0.18 | 0.11 |
| Exchangeable Mn$^{2+}$ | 0.024 | 0.065 |
| Si (%) | n.d. | 71.33 |

Note: n.d. = not determined

determined using Energy Dispersive X-ray (EDX) (JEOL JSM-IT500 HR).

### 2.4. Preparation and treatments for ammonium sorption study

The NH$_4$$^+$ sorption study was conducted in the Soil Science Laboratory at the Department of Crop Science in Universiti Putra Malaysia Bintulu Campus, Sarawak, Malaysia. A 250 g of sieved soil was weighed using electronic balance for each replicate and kept in a container prior to mixing with Calciprill and sodium silicate. In this study, the application rates of Calciprill and sodium silicate were formulated for black pepper (*Piper nigrum* L.) as our test crop. The application rates of Calciprill were fixed based on the targeted calcium saturations at 80 %, 90 %, and 100 % after which these rates were scaled down to per 250 g soil at 1.56 g (C1), 1.75 g (C2), and 1.95 g (C3), respectively [33,7]. The application rates of sodium silicate were fixed based on the average Si uptake and planting density of black pepper (*Piper nigrum* L.) at 90, 105, 120, 135, and 150 kg ha$^{-1}$ which were then converted to per 250 g soil at 1.39 g (S1), 1.62 g (S2), 1.85 g (S3), 2.08 g (S4), and 2.31 g (S5), respectively [28,3].

Three rates of Calciprill and five rates of sodium silicate were thoroughly mixed with the soil. There was a treatment as soil without any amendment (C0S0), which was used to compare the NH$_4$$^+$ sorption with the soils with the Calciprill and sodium silicate. There were another two treatments which were soils with only Calciprill at 100 % Ca saturation (C3) and sodium silicate at 150 kg ha$^{-1}$ (S5), respectively. These treatments were formulated to elucidate the separate effect of each amendment on NH$_4$$^+$ sorption of Bekenu series. There were a total of 18 treatments with three replications per treatment in these studies. Details of the treatments evaluated and their initial pH are summarized in Table 3.

### 2.5. Ammonium adsorption and desorption study

The NH$_4$$^+$ adsorption and desorption study was conducted in accordance with the procedures described by Palanivell et al. [43] and Latifah et al. [22]. A 1000 mg L$^{-1}$ isonormal NH$_4$$^+$ solution was prepared by dissolving 3.82 g of oven-dried (60 °C for 24 h) ammonium chloride ($NH_4Cl$) in 1 L of 0.2 mol dm$^{-3}$ sodium chloride (NaCl) solution. The prepared isonormal NH$_4$$^+$ solution was diluted with 0.2 mol dm$^{-3}$ NaCl into five concentrations at 0, 25, 50, 75, and 100 mg L$^{-1}$. A 2 g of soil was weighed into a 50 mL centrifuge tube and

**Table 3**
Details on treatments evaluated in the ammonium sorption study.

| Treatment | Treatment description | | Application rate | | Initial pH |
|---|---|---|---|---|---|
| | Targeted Ca saturation (%) | Rate per hectare soil (kg ha$^{-1}$) | g per 250 g soil | | |
| | | | Calciprill | Sodium silicate | |
| C0S0 | - | - | 0 | 0 | 4.27 |
| C3 | 100 | - | 1.95 | 0 | 7.30 |
| S5 | - | 150 | 0 | 2.31 | 7.45 |
| C1S1 | 80 | 90 | 1.56 | 1.39 | 7.88 |
| C1S2 | 80 | 105 | 1.56 | 1.62 | 7.75 |
| C1S3 | 80 | 120 | 1.56 | 1.85 | 7.61 |
| C1S4 | 80 | 135 | 1.56 | 2.08 | 7.96 |
| C1S5 | 80 | 150 | 1.56 | 2.31 | 7.95 |
| C2S1 | 90 | 90 | 1.75 | 1.39 | 7.56 |
| C2S2 | 90 | 105 | 1.75 | 1.62 | 7.64 |
| C2S3 | 90 | 120 | 1.75 | 1.85 | 7.68 |
| C2S4 | 90 | 135 | 1.75 | 2.08 | 7.76 |
| C2S5 | 90 | 150 | 1.75 | 2.31 | 8.05 |
| C3S1 | 100 | 90 | 1.95 | 1.39 | 7.72 |
| C3S2 | 100 | 105 | 1.95 | 1.62 | 8.02 |
| C3S3 | 100 | 120 | 1.95 | 1.85 | 7.84 |
| C3S4 | 100 | 135 | 1.95 | 2.08 | 7.95 |
| C3S5 | 100 | 150 | 1.95 | 2.31 | 7.89 |

mixed with the isonormal $NH_4^+$ solutions in a ratio of 1:10 to make soil suspensions with added 0, 250, 500, 750, and 1000 µg $NH_4^+$ $g^{-1}$ soil. The soil suspensions were shaken at 180 rpm for 24 h using an orbital shaker to reach equilibrium, followed by centrifugation at 4000 rpm for 10 min using a bench top centrifuge (Rotina 380, Hettich, North America) to obtain supernatants. The same soil samples were rinsed with 95 % ethanol through another centrifugation at 4000 rpm for 10 min to remove the residual $NH_4^+$ in soil solution. Thereafter, the ethanol was discarded and the same soil sample were used for $NH_4^+$ desorption determination by adding 20 mL of 2 mol $dm^{-3}$ KCl to desorb exchangeable $NH_4^+$ through an agitation at 180 rpm for 24 h using orbital shaker. Afterwards, the soil suspension was centrifuged at 4000 rpm for 10 min to obtain the equilibrated supernatant. The amount of $NH_4^+$ left in the supernatants after adsorption and desorption procedures was determined using steam distillation, followed by colorimeter titration [5].

### 2.6. Sorption capacities and adsorption efficiency determination

After commencing the sorption experiments, the sorption capacities and adsorption efficiency of $NH_4^+$ were calculated using the following formulae, as described by Rens et al. [49]:

$$q_e = \frac{(C_i - C_e) \times V}{w}$$

Where $q_e$ = adsorption capacity after 24 h equilibration (mg $kg^{-1}$); $C_i$ = initial concentration of $NH_4^+$ isonormal solution added (mg $L^{-1}$); $C_e$ = equilibrium concentration of $NH_4^+$ isonormal solution after 24 h (mg $L^{-1}$); V = volume of $NH_4^+$ isonormal solution added (mL); w = weight of soil sample used (g)

$$q_{de} = \frac{(C_{di} - C_{de}) \times V}{w}$$

Where $q_{de}$ = desorption capacity after 24 h equilibration (mg $kg^{-1}$); $C_{di}$ = initial concentration of $NH_4^+$ isonormal solution added ($C_i$– $C_e$) (mg $L^{-1}$); $C_{de}$ = equilibrium concentration of $NH_4^+$ isonormal solution after 24 h (mg $L^{-1}$); V = volume of $NH_4^+$ isonormal solution added (mL); w = weight of soil sample used (g).

$$\text{Adsorption efficiency} = \frac{(C_i - C_e)}{C_i} \times 100\%$$

Where $C_i$ = initial concentration of $NH_4^+$ isonormal solution added (mg $L^{-1}$) and $C_e$ = equilibrium concentration of $NH_4^+$ isonormal solution after 24 h (mg $L^{-1}$).

### 2.7. Ammonium adsorption isotherms

In this $NH_4^+$ sorption study, Langmuir and Freundlich isotherm equations were used to determine the adsorption behaviour of $NH_4^+$ in the soils with and without the application of Calciprill and sodium silicate. The collected data of $NH_4^+$ adsorption were fitted into the linear form of aforementioned isotherms and the respective parameters of each isotherm were determined to reveal which isotherm is the most suitable for describing the $NH_4^+$ adsorption mechanisms. Details on the variables and important separation factors of each isotherm are listed in Table 4.

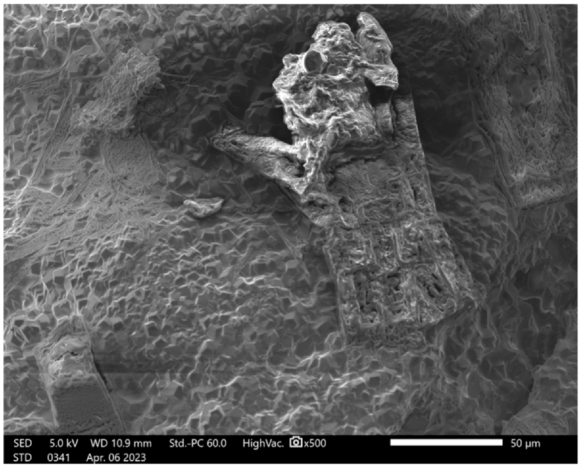

**Fig. 1.** Scanning electron monographs of Calciprill at the magnification of × 5000.

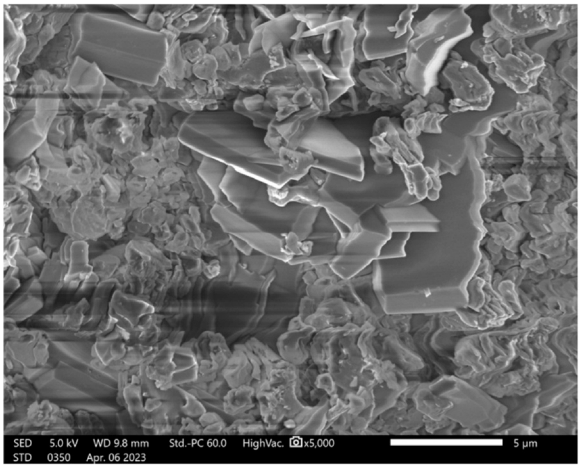

**Fig. 2.** Scanning electron monographs of sodium silicate at the magnification of × 500.

**Table 5**
Elemental composition of Calciprill and sodium silicate analyzed using Energy Dispersive X-ray.

| Elemental composition | Mass (%) | |
|---|---|---|
| | Calciprill | Sodium Silicate |
| C | 25.97 ± 0.06 | 8.29 ± 0.03 |
| O | 57.27 ± 0.18 | 57.42 ± 0.09 |
| Na | 0.51 ± 0.03 | 22.44 ± 0.07 |
| Si | 0.62 ± 0.03 | 11.85 ± 0.06 |
| S | 0.79 ± 0.03 | - |
| Ca | 14.84 ± 0.15 | - |
| Total | 100.00 | 100.00 |

**Table 4**
Details on variables and important separation factors of Langmuir and Freundlich isotherms for ammonium adsorption.

| Isotherm | Variables | Separation factor | Description |
|---|---|---|---|
| Langmuir | $K_L = \frac{intercept}{slope}$<br>$q_{\max} = \frac{1}{intercept}$ | $R_L = \frac{1}{1 + K_L C_e}$ | i. $R_L > 1$, desorption occurs after a period of adsorption<br>ii. $R_L = 1$, linear adsorption<br>iii. $R_L = 0$, irreversible adsorption |
| Freundlich | $K_F = antilog(intercept)$ $\frac{1}{n} = slope$ | $\frac{1}{n}$ | i. $n = 1$, linear adsorption<br>ii. $n < 1$, adsorption process with chemical interaction<br>iii. $n > 1$, adsorption process with physical interaction<br>iv. $0 < \frac{1}{n} < 1$, desirable adsorption<br>v. $\frac{1}{n} > 1$, cooperative adsorption occurs |

The linear form of Langmuir equation for $NH_4^+$ adsorption used in this study is presented as follow [46,8]:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L C_e}$$

Where $C_e$ = remaining amount of $NH_4^+$ left in the equilibrium solution after 24 h of equilibration (mg $L^{-1}$); $q_e$ = amount of $NH_4^+$ absorbed on the soil surfaces (adsorbent) after 24 h of equilibration (mg $g^{-1}$); $q_{max}$ = estimated maximum adsorption of $NH_4^+$ on the soil surfaces (adsorbent) after 24 h of equilibration (mg $g^{-1}$); and $K_L$ = the constant related to binding energy of $NH_4^+$ at equilibrium phase. The maximum buffering capacity was determined by multiplying $q_{max}$ and $K_L$.

The linearized adsorption equation for Freundlich isotherm is reported as follows [43,66]:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$$

Where $C_e$ = remaining amount of $NH_4^+$ left in the equilibrium solution after 24 h (mg $L^{-1}$); $q_e$ = amount of $NH_4^+$ absorbed on the soil surfaces (adsorbent) after 24 h of equilibration (mg $g^{-1}$); $K_F$ = Freundlich's adsorption constant which measures the adsorption capacity (mg $kg^{-1}$); $\frac{1}{n}$ = the constant used to determine if adsorption process is favorable when the constant in a range between 0 and 1.

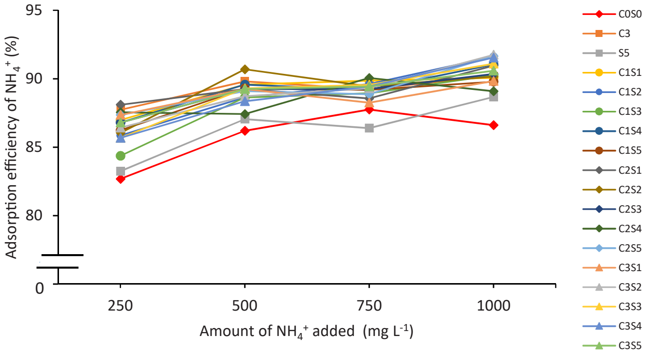

**Fig. 3.** Effects of ammonium ions addition concentrations on the adsorption efficiency of ammonium ions in relation to application of Calcipril and sodium silicate.

### 2.8. Experimental design and statistical analysis

The treatements were arranged in completely randomized design (CRD) with three replicates. The collected data were analyzed using Analysis of Variance (ANOVA) to determine the treatment effects using Generalised Linear Model (Proc GLM), thereafter mean comparison was performed using Tukey's Honestly Significant Difference (HSD) test at $p \leq 0.05$. The relationship between amount of $NH_4^+$ remaining in the equilibrium solution ($C_e$) and amount of $NH_4^+$ adsorbed by the soils

**Table 6**
Amounts of ammonium ions adsorbed in relation to application of Calciprill and sodium silicate at different amounts of ammonium ions added.

| Treatment | $NH_4^+$ adsorbed, $q_e$ (mg $kg^{-1}$) | | | |
|---|---|---|---|---|
| | Amount of $NH_4^+$ added, Ci (mg $L^{-1}$) | | | |
| | 250 | 500 | 750 | 1000 |
| C0S0 | 206.71 d<br>( ± 0.81) | 431.02 a<br>( ± 5.39) | 658.14 a<br>( ± 14.75) | 866.11 a<br>( ± 7.07) |
| C3 | 219.32 a<br>( ± 3.43) | 449.00 a<br>( ± 6.29) | 669.35 a<br>( ± 2.47) | 902.07 a<br>( ± 21.45) |
| S5 | 208.11 cd<br>( ± 1.14) | 435.23 a<br>( ± 1.87) | 647.87 a<br>( ± 9.15) | 886.66 a<br>( ± 9.15) |
| C1S1 | 217.45 ab<br>( ± 0.47) | 447.84 a<br>( ± 3.06) | 674.02 a<br>( ± 1.68) | 900.67 a<br>( ± 9.33) |
| C1S2 | 214.65 abcd<br>( ± 1.68) | 443.17 a<br>( ± 4.45) | 672.15 a<br>( ± 1.24) | 916.08 a<br>( ± 10.30) |
| C1S3 | 210.91 bcd<br>( ± 1.14) | 443.17 a<br>( ± 4.15) | 667.01 a<br>( ± 3.27) | 902.54 a<br>( ± 13.18) |
| C1S4 | 216.98 ab<br>( ± 1.87) | 447.84 a<br>( ± 5.39) | 668.88 a<br>( ± 4.58) | 910.48 a<br>( ± 10.30) |
| C1S5 | 215.58 abc<br>( ± 1.68) | 446.44 a<br>( ± 3.37) | 668.88 a<br>( ± 5.72) | 897.87 a<br>( ± 11.12) |
| C2S1 | 220.25 a<br>( ± 0.93) | 446.20 a<br>( ± 5.15) | 664.21 a<br>( ± 2.04) | 909.54 a<br>( ± 9.65) |
| C2S2 | 215.12 abc<br>( ± 1.62) | 453.44 a<br>( ± 4.15) | 670.75 a<br>( ± 8.10) | 901.60 a<br>( ± 4.45) |
| C2S3 | 216.98 ab<br>( ± 0.47) | 446.20 a<br>( ± 4.00) | 669.35 a<br>( ± 3.37) | 903.47 a<br>( ± 7.41) |
| C2S4 | 218.85 ab<br>( ± 0.47) | 437.10 a<br>( ± 4.85) | 675.42 a<br>( ± 8.95) | 890.86 a<br>( ± 4.50) |
| C2S5 | 218.38 ab<br>( ± 2.04) | 445.50 a<br>( ± 1.14) | 666.55 a<br>( ± 5.68) | 916.55 a<br>( ± 3.82) |
| C3S1 | 218.38 ab<br>( ± 1.24) | 446.20 a<br>( ± 6.29) | 661.88 a<br>( ± 6.86) | 898.33 a<br>( ± 8.18) |
| C3S2 | 216.05 abc<br>( ± 1.24) | 443.63 a<br>( ± 1.24) | 669.82 a<br>( ± 3.27) | 917.48 a<br>( ± 0.81) |
| C3S3 | 214.18 abcd<br>( ± 1.68) | 446.44 a<br>( ± 0.93) | 671.68 a<br>( ± 8.75) | 910.94 a<br>( ± 6.49) |
| C3S4 | 214.18 abcd<br>( ± 1.87) | 441.77 a<br>( ± 5.51) | 670.75 a<br>( ± 3.99) | 915.38 a<br>( ± 4.00) |
| C3S5 | 216.98 ab<br>( ± 0.93) | 446.20 a<br>( ± 1.72) | 670.75 a<br>( ± 1.68) | 905.81 a<br>( ± 4.07) |

Note: Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. Data are presented as mean ± standard error of three replicates.

**Table 7**
Regression equations, regression coefficient ($R^2$), and chi-square value for the linear relationship between the amounts of ammonium ion added and adsorbed in relation to application of Calcipril and sodium silicate using Langmuir and Freundlich isotherms.

| Treatment | Langmuir isotherm | | |
|---|---|---|---|
| | Regression equation | $R^2$ | $x^2$ |
| C0S0 | y = 0.244x − 0.001 | 0.9621 * | $1.46 \times 10^{-4}$ |
| C3 | y = 0.152x − 0.001 | 0.9811 * * | $3.98 \times 10^{-5}$ |
| S5 | y = 0.236x − 0.001 | 0.9627 * | $8.80 \times 10^{-5}$ |
| C1S1 | y = 0.170x − 0.001 | 0.9767 * * | $5.83 \times 10^{-5}$ |
| C1S2 | y = 0.212x − 0.001 | 0.9933 * * | $2.20 \times 10^{-5}$ |
| C1S3 | y = 0.233x − 0.001 | 0.9530 * | $1.46 \times 10^{-4}$ |
| C1S4 | y = 0.178x − 0.001 | 0.9734 * * | $4.11 \times 10^{-4}$ |
| C1S5 | y = 0.182x − 0.001 | 0.9659 * | $7.54 \times 10^{-5}$ |
| C2S1 | y = 0.146x − 0.0004 | 0.9872 * * | $4.41 \times 10^{-5}$ |
| C2S2 | y = 0.178x − 0.001 | $0.8459^{ns}$ | $2.73 \times 10^{-4}$ |
| C2S3 | y = 0.174x − 0.001 | 0.9843 * * | $3.42 \times 10^{-5}$ |
| C2S4 | y = 0.153x − 0.0003 | 0.9802 * * | $5.41 \times 10^{-5}$ |
| C2S5 | y = 0.167x − 0.001 | 0.9807 * * | $7.08 \times 10^{-5}$ |
| C3S1 | y = 0.155x − 0.0004 | 0.9820 * * | $4.20 \times 10^{-5}$ |
| C3S2 | y = 0.195x − 0.001 | 0.9875 * * | $4.72 \times 10^{-5}$ |
| C3S3 | y = 0.210x − 0.001 | 0.9678 * | $6.92 \times 10^{-5}$ |
| C3S4 | y = 0.216x − 0.001 | 0.9938 * * | $2.74 \times 10^{-5}$ |
| C3S5 | y = 0.177x − 0.001 | 0.9869 * * | $2.89 \times 10^{-5}$ |
| **Treatment** | **Freundlich isotherm** | | |
| | **Regression equation** | $R^2$ | $x^2$ |
| C0S0 | y = 1.293x + 0.231 | 0.9595 * | $2.18 \times 10^{-3}$ |
| C3 | y = 0.608x + 1.177 | 0.9845 * * | 0.358 |
| S5 | y = 1.352x + 0.145 | 0.9626 * | $2.20 \times 10^{-3}$ |
| C1S1 | y = 1.268x + 0.441 | 0.9869 * | $7.19 \times 10^{-4}$ |
| C1S2 | y = 1.585x − 0.130 | 0.9765 * * | $1.21 \times 10^{-3}$ |
| C1S3 | y = 1.529x − 0.085 | 0.9757 * * | $1.40 \times 10^{-3}$ |
| C1S4 | y = 1.341x + 0.313 | 0.9688 * | $8.07 \times 10^{-3}$ |
| C1S5 | y = 1.281x + 0.389 | 0.9801 * * | $1.11 \times 10^{-3}$ |
| C2S1 | y = 1.168x + 0.622 | 0.9571 * | $2.10 \times 10^{-3}$ |
| C2S2 | y = 1.257x + 0.461 | 0.8973 * | $5.92 \times 10^{-3}$ |
| C2S3 | y = 1.291x + 0.387 | 0.9897 * * | $5.53 \times 10^{-4}$ |
| C2S4 | y = 1.150x + 0.619 | 0.9601 * | $2.05 \times 10^{-3}$ |
| C2S5 | y = 1.314x + 0.368 | 0.9338 * | $3.31 \times 10^{-3}$ |
| C3S1 | y = 1.144x + 0.636 | 0.9761 * * | $4.63 \times 10^{-3}$ |
| C3S2 | y = 1.486x + 0.054 | 0.9518 * | $2.46 \times 10^{-3}$ |
| C3S3 | y = 1.515x − 0.008 | 0.9792 * * | $1.14 \times 10^{-3}$ |
| C3S4 | y = 1.587x − 0.145 | 0.9714 * | $1.48 \times 10^{-3}$ |
| C3S5 | y = 1.587x + 0.331 | 0.9917 * * | $4.43 \times 10^{-3}$ |

Note: $R^2$ values with an asterisk (*) and two asterisks (**) indicate the relationship by linear regression is significant at a confidence level of 95 % and 99 % respectively, whereas ns represents not significant.

($q_e$) was determined using simple linear regression (Proc Reg) to obtain R-square ($R^2$) value and regression equation. The software used was Statistical Anaalysis System (SAS) version 9.4, Cary, NC, USA. To select the best-fit isotherm model among Langmuir and Freundlich isotherm models for describing the $NH_4^+$ adsorption, chi-square was used to determine which isotherm model will reveal a lower chi-square value using the following formula [42]:

$$x^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$$

Where $q_e$ is the adsorption capacity of $NH_4^+$ obtained from the sorption study, whereas $q_{e,m}$ is the adsorption capacity computed from the isotherm model.

## 3. Results and discussion

### 3.1. Surface morphology and elemental composition of Calcipril and sodium silicate

The SEM analysis revealed that the Calcipril has a mix of amorphous surfaces and irregular crystalline structures which are in the forms of quadrilateral, cubic, and prismatic shapes (Fig. 1). The irregular crystalline structure of Calcipril had a particle size ranging from approximately 2.17 µm to 6.33 µm. Compared with Calcipril, the morphological surface of the sodium silicate is rough and amorphous because no visible crystalline structure was observed (Fig. 2). In terms of porosity, unlike charcoal and sago bark ash as reported by Johan et al. [19], there was no visible pores observed on the surfaces of Calcipril and sodium silicate under the scanning electron monographs, regardless of magnification.

Table 5 summarizes the elemental composition of Calcipril and sodium silicate using EDX. The EDX analysis demonstrated that the elemental composition of Calcipril by mass percentage was in the descending order of: O (57.27 %), C (25.97 %), Ca (14.84 %), S (0.79 %), Si (0.62 %), and Na (0.51 %). Also, the sodium silicate had the highest O content by mass percentage of 57.42 %, followed by Na (22.44 %), Si (11.85 %), and C (8.29 %). This finding verifies that sodium silicate ($NaSiO_3$) is a synthetic fertilizer which will break down into $Na^+$ and $SiO_3^{2-}$ ions when it is in contact with the soil water. The presence of C in both Calcipril and sodium silicate is due to the C sequestration as contaminants during the mineral precipitation of amendments [58]. The presence of Na indicates that both amendments might contain sodium carbonate ($Na_2CO_3$) which has crystalline decahydrate structure [36]. Notably, compared with Calcipril, the higher Na content in the sodium silicate suggests that it is more salty and could dominantly affect soil salinity. In addition, the presence of highest substantial O reveals that the amendments have mineral oxides [9]. The finding on the presence of Si and S in Calcipril is in agreement with that of Ma et al. [26] who reported that carbonaceous rocks such as limestone might have impurities such as mineral clays and silica. Additionally, the presence of S in Calcipril suggests that the amendment might have aragonite, which is a naturally occurring carbonate mineral that is made up of sulphates ($SO_4^{2-}$) [62].

### 3.2. Soil ammonium adsorption following application of Calcipril and sodium silicate

Effects of Calcipril and sodium silicate on the amounts of adsorbed $NH_4^+$ at the adding concentrations of 250, 500, 750, and 1000 mg L$^1$ after 24 h equilibration are presented in Table 6. At lower concentration of $NH_4^+$ addition (250 mg L$^1$), the application of Calcipril only (C3) and combined use of Calcipril and sodium silicate (C1S1, C1S4, C1S5, C2S1, C2S2, C2S3, C2S4, C2S5, C3S1, C3S2, and C3S5) significantly improved the adsorption of $NH_4^+$ ions to a range of 215.12 mg kg$^{-1}$ to 220.25 mg kg$^{-1}$ compared with that of the soil without amendment (C0S0) at 206.71 mg kg$^{-1}$. Besides, the soil with sodium silicate only (S5) did not significantly increase $NH_4^+$ adsorption compared to that of the soil without amendment (C0S0) because of the high solubility of sodium silicate when in contact with soil water, which does not significantly increase negatively charged sites to adsorb $NH_4^+$. This comparison suggests that Calcipril is an effective adsorbent that dominantly improves $NH_4^+$ adsorption relative to sodium silicate. The lowest $NH_4^+$ adsorption observed in the soils without amendment (C0S0) was due to the acidic pH value (4.27), which stimulates competition between $NH_4^+$ and high concentration of $H^+$ to be adsorbed at the negatively charged sites. This finding is consistent with that of Sharifnia et al. [56] who opined that the high $H^+$ ions concentration under low pH conditions (pH < 5) can outcompete the $NH_4^+$ from being adsorbed at the negatively charged exchangeable sites of soil colloids. Furthermore, the lower $NH_4^+$ adsorption is related to lower negative charge density because the strong hydrogen bond between the 1:1 lattice aluminium-silicate sheets of kaolinite clay minerals in Bekenu series causes low CEC [34].

In contrast, the improved $NH_4^+$ adsorption in the soils with co-application of Calcipril and sodium silicate was due to the increased pH. According to Fidel et al. [13], $NH_4^+$ adsorption correlates positively with soil pH because of the increased number of negative charged

**Table 8**
Parameters estimated by Freundlich isotherm for ammonium adsorption in relation to treatments.

| Treatment | Parameters estimated by Freundlich isotherm | |
|---|---|---|
| | $K_F$ (mg $kg^{-1}$) | $\frac{1}{n}$ |
| C0S0 | 1.703 | 1.293 |
| C3 | 15.015 | 0.608 |
| S5 | 1.397 | 1.352 |
| C1S1 | 2.758 | 1.268 |
| C1S2 | 0.742 | 1.585 |
| C1S3 | 0.822 | 1.529 |
| C1S4 | 2.057 | 1.341 |
| C1S5 | 2.449 | 1.281 |
| C2S1 | 4.192 | 1.168 |
| C2S2 | 2.889 | 1.257 |
| C2S3 | 2.435 | 1.291 |
| C2S4 | 4.160 | 1.150 |
| C2S5 | 2.334 | 1.314 |
| C3S1 | 4.327 | 1.144 |
| C3S2 | 1.133 | 1.486 |
| C3S3 | 0.982 | 1.515 |
| C3S4 | 0.717 | 1.587 |
| C3S5 | 2.144 | 1.326 |

exchangeable sites to adsorb more $NH_4^+$ and the maximum $NH_4^+$ adsorption occurs in a pH range of 7 to 7.5. However, when the pH is higher than 8, the adsorption capacity of $NH_4^+$ is significantly reduced because exchangeable $NH_4^+$ transforms into $NH_3$ by urease through volatilization [1,6]. Therefore, these findings suggest that the use of Calcipril and sodium silicate should be optimized to prevent $NH_3$ volatilization. In addition, the amendments improved $NH_4^+$ adsorption through increased soil ECEC when the pH increases to stimulate deprotonation. This reaction increased negatively-charged surfaces on the soil colloids to absorb more $NH_4^+$ ions. For example, the dissolution of Calciprill increases $CO_3^{2-}$ concentration as negatively charged exchangeable sites, causes higher retention of $NH_4^+$ in the soil through electrostatic attraction [48]. Moreover, the base cations released into the soil solution through dissolution caused ion exchange at the exchangeable sites to retain more $NH_4^+$. The improved $NH_4^+$ adsorption using the amendments can also mitigate environmental pollution such as eutrophication because of the reduced nitrification and leaching of $NO_3^-$ [37,38].

The amendments did not significantly increase $NH_4^+$ adsorption compared with the soil without amendment (C0S0) at higher $NH_4^+$ loadings (500, 750, and 1000 mg $L^{-1}$), suggesting that the Calciprill and sodium silicate did not maximize $NH_4^+$ adsorption with increasing $NH_4^+$ addition. In contrast, the improved $NH_4^+$ adsorption at the lower concentration of $NH_4^+$ added (250 mg $L^{-1}$) indicates that the effects of the combined use of Calciprill and sodium silicate on $NH_4^+$ adsorption are more pronounced in the soils with the lower $NH_4^+$ content. Although the amendments did not improve $NH_4^+$ adsorption at higher $NH_4^+$ loadings (500, 750, and 1000 mg $L^{-1}$), the amount of $NH_4^+$ adsorbed ($q_e$) gradually increased with the increasing initial

**Table 9**
Amounts of ammonium ions desorbed in relation to application of Calciprill and sodium silicate at different amounts of ammonium ions added.

| Treatment | $NH_4^+$ desorbed into the equilibrium solution (mg $L^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Amount of $NH_4^+$ added, Ci (mg $L^{-1}$) | | | | |
| | 0 | 250 | 500 | 750 | 1000 |
| C0S0 | 16.67 a<br>( ± 3.71) | 12.00 a<br>( ± 1.68) | 16.20 ab<br>( ± 0.47) | 19.01 ab<br>( ± 0.47) | 18.54 abc<br>( ± 0.47) |
| C3 | 11.53 ab<br>( ± 0.93) | 11.07 a<br>( ± 0.81) | 13.40 ab<br>( ± 0.47) | 13.87 b<br>( ± 1.14) | 14.80 bc<br>( ± 1.24) |
| S5 | 9.20 b<br>( ± 0.47) | 13.40 a<br>( ± 1.68) | 10.37 b<br>( ± 1.72) | 22.28 a<br>( ± 0.81) | 20.41 abc<br>( ± 1.87) |
| C1S1 | 9.20 b<br>( ± 1.24) | 14.34 a<br>( ± 0.47) | 15.74 ab<br>( ± 0.47) | 19.47 ab<br>( ± 1.14) | 13.40c<br>( ± 0.93) |
| C1S2 | 9.67 b<br>( ± 0.81) | 13.40 a<br>( ± 0.93) | 16.67 ab<br>( ± 1.62) | 18.07 ab<br>( ± 2.14) | 20.87 abc<br>( ± 0.81) |
| C1S3 | 10.13 b<br>( ± 1.24) | 13.87 a<br>( ± 0.81) | 18.54 a<br>( ± 1.68) | 19.01 ab<br>( ± 2.60) | 22.98 a<br>( ± 0.57) |
| C1S4 | 9.67 b<br>( ± 0.00) | 13.87 a<br>( ± 0.00) | 19.01 a<br>( ± 1.68) | 16.67 ab<br>( ± 2.14) | 18.07 abc<br>( ± 1.40) |
| C1S5 | 9.67 b<br>( ± 0.00) | 13.40 a<br>( ± 1.24) | 16.67 ab<br>( ± 1.40) | 19.94 ab<br>( ± 0.47) | 21.58 ab<br>( ± 0.57) |
| C2S1 | 8.73 b<br>( ± 0.47) | 13.87 a<br>( ± 0.81) | 14.34 ab<br>( ± 2.04) | 18.07 ab<br>( ± 0.81) | 18.07 abc<br>( ± 1.62) |
| C2S2 | 10.60 b<br>( ± 0.93) | 13.40 a<br>( ± 0.47) | 18.07 ab<br>( ± 1.40) | 17.61 ab<br>( ± 1.68) | 20.87 abc<br>( ± 2.14) |
| C2S3 | 9.67 b<br>( ± 0.00) | 12.47 a<br>( ± 0.00) | 17.14 ab<br>( ± 0.47) | 19.47 ab<br>( ± 0.81) | 19.47 abc<br>( ± 0.81) |
| C2S4 | 10.13 b<br>( ± 0.47) | 12.94 a<br>( ± 0.47) | 14.80 ab<br>( ± 1.68) | 15.74 ab<br>( ± 1.87) | 19.47 abc<br>( ± 1.14) |
| C2S5 | 11.07 ab<br>( ± 0.00) | 12.94 a<br>( ± 0.47) | 14.34 ab<br>( ± 2.34) | 19.47 ab<br>( ± 0.81) | 13.87 bc<br>( ± 1.14) |
| C3S1 | 9.67 b<br>( ± 1.40) | 12.47 a<br>( ± 0.81) | 16.20 ab<br>( ± 0.47) | 15.27 ab<br>( ± 0.81) | 16.20 abc<br>( ± 1.24) |
| C3S2 | 9.20 b<br>( ± 0.47) | 12.94 a<br>( ± 0.93) | 16.20 ab<br>( ± 1.68) | 17.14 ab<br>( ± 0.47) | 19.94 abc<br>( ± 2.60) |
| C3S3 | 8.73 b<br>( ± 0.47) | 12.47 a<br>( ± 0.81) | 15.74 ab<br>( ± 2.60) | 17.61 ab<br>( ± 0.93) | 15.27 abc<br>( ± 1.40) |
| C3S4 | 10.60 b<br>( ± 0.47) | 12.47 a<br>( ± 1.62) | 16.20 ab<br>( ± 0.47) | 18.54 ab<br>( ± 0.47) | 17.37 abc<br>( ± 0.57) |
| C3S5 | 10.60 b<br>( ± 0.47) | 12.00 a<br>( ± 0.47) | 14.34 ab<br>( ± 0.47) | 14.80 b<br>( ± 0.93) | 17.14 abc<br>( ± 1.24) |

Note: Different letters indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. Data are presented as mean ± standard error of three replicates.

concentrations of $NH_4^+$ added ($C_i$) (Fig. 3) because of the influence of initial $NH_4^+$ concentrations added and sufficient exchangeable sites at the absorbent to retain more $NH_4^+$. This finding is comparable to that of Latifah et al. [22] who reported that the adsorption of $NH_4^+$ by clinoptilolite zeolite increases with the increasing initial concentrations of $NH_4^+$ isonormal solutions at 18, 180, 450, and 900 mg L$^{-1}$, suggesting that the initial concentrations of $NH_4^+$ added also influence $NH_4^+$ adsorption efficiency. Furthermore, the finding corroborates that of Song et al. [57] who demonstrated that the increased adsorption of $Cu^{2+}$ ions by porous vaterite and cubic aggregated $CaCO_3$ at increasing initial $Cu^{2+}$ concentrations of 300 to 1100 mg L$^{-1}$ was due to the adequate number of adsorption sites of the adsorbent.

### *3.3. Langmuir and Freundlich adsorption isotherms of ammonium ions*

The linear relationship between the amount of $NH_4^+$ added and the amount of $NH_4^+$ adsorbed by the soil with or without the amendments using Langmuir and Freundlich isotherms are presented in Table 7. Although the Langmuir isotherm exhibited lower chi-square values compared with the Freundlich isotherm, the negative intercepts of the regression equations suggest that the $NH_4^+$ adsorption by Calciprill and sodium silicate did not follow the assumptions of Langmuir isotherm. Conversely, the positive intercepts in the regression equations (except for C1S2, C1S3, C3S3, and C3S4) of Freundlich isotherms indicate that it is the most suitable isotherm which describes $NH_4^+$ adsorption. According to Dada et al. [12], in Freundlich adsorption isotherm, $NH_4^+$ ions bind on the soil negatively charged exchangeable sites which are heterogeneous in nature and the $NH_4^+$ ions can further adsorb to one another in two or more layers through the formation of weak bonds.

The parameters estimated by Freundlich isotherm on $NH_4^+$ adsorption of the acid soil (Bekenu series) amended with or without Calciprill and sodium silicate are demonstrated in Table 8. According to Mbuvi et al. [31], adsorption capacity ($K_F$) is a constant that is used to estimate the amount of adsorbed $NH_4^+$ ions that are released into the solution from the holding sites for crop uptake. Notably, the soil with Calciprill only (C3) exhibited higher $K_F$ value (15.015) compared with the soil without any amendment (C0S0) ($K_F$ value of 1.703). Besides, the addition of sodium silicate only (S5) slightly reduced the $K_F$ to 1.397 compared with the soil without any amendment (C0S0). This finding is consistent with the preceding finding, which suggests that Calciprill has the ability to adsorb higher amount of $NH_4^+$ ions. However, the $K_F$ values of the soil with the combined use of Calciprill and sodium silicate did not increase with the increasing amount of the amendments because of the inconsistent dissolution of Calciprill. This was possible because the dissolution of sodium silicate liberates silicate ions to stabilize the soil structure through the formation of silica gel between the soil pores, thus reducing soil permeability and preventing the dissolution of Calciprill [35,27].

The 1/n constant is a parameter that is used to determine the variations of buffering capacity of $NH_4^+$ in a soil [29,31]. The fact that the soil with Calciprill only (C3) had 1/n value of 0.608 (lower than 1) suggests that the occurrence of adsorption of $NH_4^+$ ions is favourable and with greater heterogeneity. In contrast, the 1/n values which are greater than 1 of the other treatments indicate that the adsorption of $NH_4^+$ is unfavourable and cooperative. According to Liu [25], cooperative adsorption is the deviation from Langmuir isotherm wherein the adsorbed adsorbates on the surface of an absorbent have an interaction with the free moving adsorbate in the soil solution, resulting in the occurrence of multilayer adsorption.

### *3.4. Soil ammonium desorption following application of Calciprill and sodium silicate*

Effects of the Calciprill and sodium silicate on the amounts of desorbed $NH_4^+$ at 0, 250, 500, 750, and 1000 mg L$^{-1}$ after 24 h equilibration are presented in Table 9. Unlike $NH_4^+$ adsorption, amending the soil with Calciprill and sodium silicate did not significantly influence the desorption of $NH_4^+$ relative to the soil without any amendment (C0S0) at lower concentration of $NH_4^+$ addition (250 mg L$^{-1}$). Moreover, the desorption of $NH_4^+$ did not consistently increase at higher $NH_4^+$ concentrations of 500, 750, and 1000 mg L$^{-1}$, although some treatments (C0S0, S5, C1S1, C1S4, C2S2, C2S5, C3S1, C3S3, and C3S4) showed a fluctuation trend. This is related to the fluctuations of adsorption capacity ($K_F$) (Table 8) because of the inconsistent dissolution of Calciprill to release $NH_4^+$, suggesting that the Calciprill is a durable soil amendment which has higher affinity to adsorb $NH_4^+$. Moreover, the combined use of Calciprill and sodium silicate might have protected the $NH_4^+$ ions from losses through leaching, nitrification, and $NH_3$ volatilization because of the soil stabilization. This is because Gezerman [15] reported that the addition of $CaCO_3$ and sodium silicate can prevent the degradation and caking of ammonium nitrate fertilizer because the reaction stimulates the formation of stabilized crystal structure on the surface of fertilizer.

## 4. Conclusions

It is possible to mitigate N pollution in soil water through amending $NH_4^+$ sorption in acid soils using Calciprill and sodium silicate because of the increased pH and number of negatively charged sites in addition to improving structure and reducing permeability of the amended soil. The combined use of Calciprill and sodium silicate significantly improves $NH_4^+$ adsorption at lower $NH_4^+$ application (250 mg L$^{-1}$), but not at higher $NH_4^+$ loadings (500, 750, and 1000 mg L$^{-1}$), suggesting that effects of amendments are more pronounced in the soils with lower N content to prevent N contamination in water bodies. The $NH_4^+$ adsorption follows the assumption of Freundlich isotherm where the $NH_4^+$ ions bind on the soil negatively charged exchangeable sites which are heterogeneous in nature and the $NH_4^+$ ions can further adsorb to one another in two or more layers through the formation of weak bonds. The effects of Calciprill and sodium silicate on $NH_4^+$ desorption remain unclear, which could be because of the ability of sodium silicate to stabilize soil structure and permeability, thus temporarily fixing $NH_4^+$ from being lost through surface runoff and leaching because of the inconsistent dissolution of Calciprill. However, the limitation of this sorption study is that the application rates of N fertilizer were not based on the prevailing fertilization method because of the absence of black pepper plant as our test crop. Therefore, pot trial is recommended to elucidate N interactions with the black pepper plant grown on the soil following the application of Calciprill and sodium silicate.

## Funding

This research was funded by Humibox Sdn. Bhd., Kuala Lumpur, Malaysia (Grant number: 6300920) and Omya Asia Pacific Sdn. Bhd., Kuala Lumpur, Malaysia (Grant number: 6300923).

## CRediT authorship contribution statement

Conceptualization, J.F.N. and O.H.A.; methodology, J.F.N., O.H.A., R.W., and D.R.J.; investigation, J.F.N.; resources, A.A.M.; writing—original draft preparation, J.F.N.; writing—review and editing, O.H.A., L.O., M.B.J., and A.J.K.C.; visualization, J.F.N.; supervision, O.H.A. L.O., M.B.J., and Y.M.K.; project administration, O.H.A., L.O., M.B.J., and A.A.M.; funding acquisition, O.H.A., L.O., M.B.J., and A.A.M. All authors have read and agreed to the published version of the manuscript.

## Data Availability

The data presented in this study are available within the article.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

The authors would like to thank Humibox Sdn. Bhd., Kuala Lumpur, Malaysia (Grant number: 6300920) and Omya Asia Pacific Sdn. Bhd., Kuala Lumpur, Malaysia (Grant number: 6300923) for funding this research project. The authors would also thank Universiti Putra Malaysia (Malaysia), Universiti Malaysia Sabah (Malaysia), Management and Science University (Malaysia), Universiti Malaysia Sarawak (Malaysia), and Universiti Islam Sultan Sharif Ali (Brunei Darussalam) for the research collaboration.

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