Novel nano-submicron mineral-based soil conditioner for sustainable agricultural development

Shanke Liu\textsuperscript{a},*, Xin Qi\textsuperscript{b}, Cheng Han\textsuperscript{a}, Jianming Liu\textsuperscript{a,\textsuperscript{**}}, Xuebin Sheng\textsuperscript{c}, He Li\textsuperscript{d}, Anming Luo\textsuperscript{e}, Jianglin Li\textsuperscript{f}

\textsuperscript{a} Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China
\textsuperscript{b} School of Life Sciences, Tsinghua University, Beijing, 100084, China
\textsuperscript{c} Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
\textsuperscript{d} State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China
\textsuperscript{e} Zhongke Jiancheng Mineral Technology (Beijing) Co., Ltd., Beijing, 100029, China
\textsuperscript{f} Agricultural Bureau of Liling City, Liling, 412200, Hunan Province, China

\textbf{Article info}

\textbf{Article history:}
Received 21 December 2016
Received in revised form 21 February 2017
Accepted 21 February 2017
Available online 24 February 2017

\textbf{Keywords:}
Environmentally friendly
Hydrothermal
Nano-submicron
Mineral-based
Soil remediation

\textbf{Abstract}

Soil is formed through the weathering of natural rocks, and the solid composition of soil is at least 90% minerals. Soil experiences acidification and heavy metal contamination, and these phenomena are global problems that must be addressed on the basis of green chemistry principles to achieve sustainable agricultural development and maintain a healthy ecological environment. Soil may be effectively remediated by applying mineral-based soil conditioners. In this study, soil formation was simulated and a novel nano-submicron mineral-based soil conditioner was prepared from a potassium-rich feldspar by using an environmentally friendly hydrothermal method to buffer severe acidification and inhibit the phytoavailability of hazardous elements in soil. Field and in-house experiments confirmed that the performance of the proposed soil conditioner as soil amendment was effective. Soil pH was improved by 1%–9% compared with that of the control group, and soil bulk density decreased by approximately 8%. Al concentration in soil decreased by 29%–42% compared with that of the control group, and this observation indicated that aluminum toxicity was alleviated. Cd concentration in the corn of the rice also decreased by 50% compared with the control level, and this result suggested that cadmium accumulation was inhibited. This excellent performance was attributed to multifactor synergy and closely related to the morphology, chemical composition, mineral components, and preparation method of the proposed soil conditioner.

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\textbf{1. Introduction}

Soil acidification is a major problem in intensive agricultural systems in China (Guo et al., 2010; Lu et al., 2014). Consequently, China is under great pressure because it feeds 21% of the world’s population with 8% of the world’s arable land. In addition to surface and groundwater pollution and greenhouse gas emissions, the excessive application of nitrogen (N) fertilizers has caused significant soil acidification in major Chinese croplands and has consequently decreased soil pH by 0.13–2.20 (Guo et al., 2010; Miao et al., 2011). China contributes to up to 35% of the total global fertilizer consumption at a fertilizer consumption rate of 318.5 kg ha\textsuperscript{-1} (CMAO, 2015), and this value is much higher than the global average of 120 kg ha\textsuperscript{-1}. The country’s use versus output is 2.6 times that of the United States and 2.5 times that of the European Union. As a result, redundant fertilizer N is lost to the environment and subsequently induces negative environmental impacts. Therefore, China targets zero growth in chemical fertilizer use by 2020 via optimal strategies (CMAO, 2015), including a good drainage and effective water management system (Valipour, 2012, 2015), nutrient-balance fertilization and increased fertilizer utilization rates (Chen et al., 2006; Ju et al., 2009; Miao et al., 2011; Peng et al., 2010); these strategies provide multiple benefits to the agriculture and the environment but do not decrease crop yield.

The anthropogenic acidification of croplands is not easily...
alleviated within a short period because China should continuously prioritize the application of high amounts of chemical fertilizers to maintain high yields. Soil acidification may be slowed down by improving soil quality, which is a key factor in preventing soil degradation (Cassman, 1999) caused by increased fertilizer utilization (Chen et al., 2006; Ju et al., 2009; Miao et al., 2011; Peng et al., 2010). This condition exacerbates in the occurrence of certain phenomena, including contamination of hazardous elements, such as aluminum (Al) (Marshner, 1991; Wen et al., 2014), which are primary limiting factors in acidic soil (Kochian et al., 2004), or heavy metals (Kirkham, 2006; Liao et al., 2005; Sukreeyapongse et al., 2002), which become labile with enhanced soil acidity. For example, cadmium (Cd) contamination in rice has further raised concerns regarding potential risks caused by heavy metals in China (Ke et al., 2015).

Soil is formed through the weathering of natural rocks, and the solid composition of soil is at least 90% minerals. Soil may be effectively remediated by applying mineral-based soil conditioners. Amending soil with mineral-based materials, including natural and synthetic minerals, has been thoroughly reviewed (Kogbara, 2014; Koptsik, 2014; O’Day and Vlassopoulos, 2010; Ram and Masto, 2014). Some minerals can be effective in amending soils, especially stabilizing/solidifying heavy metals and improving soil pH. These substances include natural or modified minerals, such as zeolite (Shaheen and Rinklebe, 2015), clay (Shaheen and Rinklebe, 2015), quicklime (Cao et al., 2008; Shaheen and Rinklebe, 2015), limestone (Shaheen and Rinklebe, 2015), and artificial minerals, such as cement or cement-like binder (Cao et al., 2008; Shaheen and Rinklebe, 2015; Yoon et al., 2010), and fly ash (Ram and Masto, 2014; Shaheen and Rinklebe, 2015; Shi et al., 2009; Weber et al., 2015). Most of these materials perform single functions and contain trace or no nutrient element that can be available for plants. Some materials, especially fly ash, are potentially used for soil amendments because of their good properties, but these materials are likely enriched by contaminants, including salts and heavy metals (Ram and Masto, 2014 and references therein). Their application poses a contamination risk to soil, plants, and surface and ground water because of the increased concentrations of potentially toxic heavy metals. Minerals with a CaO–Al2O3–SiO2 (CAS) chemical component, such as cement, may cause soil compaction after application because CAS hydration reaction occurs.

The mobility of fixed colloidal metals is significant and is increased as soil pH is decreased (Lombi et al., 2003). As such, alkaline soil amendments must be considered to increase soil pH. Liming is commonly practiced to overcome the effect of soil acidification (Bolan and Hedley, 2003), but the use of liming has become limited since the mid-1980s because of its economic cost and operability. Lime application is beneficial to crops and soil (Fageria and Baligar, 2008; Li et al., 2014; Paradelo et al., 2015), but its net effect on soil remains unclear (Paradelo et al., 2015).

In some instances, available mineral-based soil conditioners are unsatisfactory and thus should be further improved for sustainable agricultural development in China and other countries. In this study, soil formation was simulated by applying an environmentally friendly hydrothermal technique for the first time and producing a nano-submicron mineral-based soil conditioner (NMSC) from a potassium-rich feldspar. This study aimed to buffer severe acidification and alleviate the toxicity of harmful elements in red soil in South China by investigating the changes in pH, activated Al concentration, and Cd levels after NMSC application.

2. Experimental method

2.1. Preparation of the NMSC

By simulating the natural weathering of rocks, we generated a NMSC through an environmentally friendly hydrothermal reaction between potassium-rich feldspar and lime. The detailed experimental conditions are listed in Table 1. Given the chemical compositions of the raw materials and the requirements for NMSC, we can control and adjust the relaxed reaction conditions. For example, 60% potassium-rich feldspar and 40% lime were subjected to a hydrothermal atmosphere at 190 °C for 10 h to produce the desired material. The selected chemical components and hazardous elements of the industrial production are listed in Table S1.

2.2. Pot-culture experiment

A certain amount of red soil was sampled from the topsoil (0–30 cm) in the Red Soil Institute in Jinxian County, Jiangxi Province, China (28° 21’ N, 116° 10’ E). The physicochemical properties of the sample are listed in Table S2. Pot-culture experiments were conducted in a greenhouse in the College of Resources and Environment of China Agricultural University. A bucket with a diameter of 15 cm and a height of 20 cm was chosen as a soil container. Considering our different objectives, we designed two groups of pot-culture experiments.

2.2.1. First group of pot-culture experiments

In each pot, 5 kg of red soil was mixed with 0.1 g kg⁻¹ N per soil sample (equivalent to 225 kg ha⁻¹ pure N), 0.1 g kg⁻¹ P₂O₅ per soil sample (equivalent to 225 kg ha⁻¹ P₂O₅), and 0.05 g kg⁻¹ K₂O per soil sample (equivalent to 122.5 kg hm⁻² K₂O). N, phosphorus (P), and potassium (K) fertilizers corresponded to urea (46% N), diammonium phosphate (DOP; 46% P₂O₅ and 18% N), and potassium sulfate (SOP; 54% K₂O), respectively. Urea was applied in four different stages: 40% as basal fertilizer, 20% as tillering fertilizer, 30% as earing fertilizer, and 10% as ripening fertilizer. Aluminum sulfate hydrate (Al₂(SO₄)₂·18H₂O) as an Al resource was added to the pot; its Al concentration was 0.1 mg kg⁻¹ Al per soil sample. Al was added after the rice seedlings were transplanted. Four treatments were designed (Table 2). Of the four treatment groups, two were not administered with NMSC and the two other groups were applied with NMSC. Each treatment was quadruplicated, and all of the buckets were randomly arranged. The NMSC contents in the four treatments were equivalent to 0, 0, 450, and 900 kg ha⁻¹, respectively.

2.2.2. Second group of pot-culture experiments

In each pot, 10 kg of red soil was mixed with 0.1 g kg⁻¹ N per soil sample (equivalent to 225 kg ha⁻¹ pure N), 0.1 g kg⁻¹ P₂O₅ per soil sample (equivalent to 225 kg ha⁻¹ P₂O₅), 0.05 g kg⁻¹ K₂O per soil sample (equivalent to 122.5 kg ha⁻¹ K₂O). N, P, and K fertilizers corresponded to urea (46% N), DOP (46% P₂O₅, 18% N), and SOP (54% K₂O), respectively. Urea was applied in four different stages: 40% as

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<th>Table 1</th>
<th>Preparation of the nano-submicron mineral-based soil conditioner.</th>
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<tr>
<td>Potassium-rich feldspar (%)</td>
<td>Lime (%)</td>
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2.4. Measurement of physicochemical properties shown in Table S3. Early- and late-maturing rice samples (Rice quaternary red clay. The soil's main physicochemical properties are soil was composed of yellow clayey paddy soil developed from soil samples were collected and analyzed. Six plots (each plot was variety, Guyou 3119) were continuously planted in the plots in the rice seedlings were transplanted, 150 kg ha⁻¹ / C⁰, respectively. Each plot was separately sampled and disposed. The soil sample in each plot was also individually collected from the topsoil season, each plot was separately sampled and disposed. The soil

2.3. Field test

Field test plots were located in Xiaquan Village in Taoshui Town in Youxian County, Hunan Province, China (27° 0' N, 113° 20' E). The soil was composed of yellow clayey paddy soil developed from quaternary red clay. The soil’s main physicochemical properties are shown in Table S3. Early- and late-maturing rice samples (Rice variety, Guyou 3119) were continuously planted in the plots in 2014, but only the late-maturing rice samples and corresponding soil samples were collected and analyzed. Six plots (each plot was 33 m² in area) were arranged in a randomized complete block experimental design with three replicates. Two treatments were designed: Treatment 1 (control) with conventional fertilization and Treatment 2 with conventional fertilization and 1500 kg ha⁻¹ NMSC.

All of the plots were managed with the same procedures, and 375 kg ha⁻¹ conventional fertilization with 40% nutrient (N:P:K = 5:2:3) was applied as the basal fertilizer. One week after the rice seedlings were transplanted, 150 kg ha⁻¹ urea and 75 kg ha⁻¹ potassium chloride were applied. During the harvest season, each plot was separately sampled and disposed. The soil sample in each plot was also individually collected from the topsoil (0–30 cm).

2.4. Measurement of physicochemical properties

Three or four replicates were prepared for the pot-culture experiments and the field test. All of the relevant parameters of each replicate were individually determined, and average values of corresponding multiple replicates were presented for brevity.

2.4.1. pH measurement

Previous studies confirmed that the pH obtained by different methods slightly differed but the pH values obtained by the same procedure were comparable (Thunjai et al., 2001; Wang et al., 2015b). All soil samples were air dried at 60 °C in a forced-draft oven and sieved to sizes less than 2 mm prior to analysis. The soil and distilled water were mixed in a 1:5 ratio (weight:volume). After 30 min of end-over-end shaking, the pH was measured by a three-point calibration buffer method (pH = 4.01, 6.87, 9.18) with a Eutech pH 11 m (Oakton, USA).

2.4.2. Al measurement in soil

Al is abundant in soil and mostly present in insoluble forms at above pH = 5.0. However, the enhanced solubility and mobility of Al in acidic environments has become a potential hazard to plants. The forms of extractable soil Al are diverse and exert different effects on plants (Soon, 1995). To evaluate this potential hazard, we extracted the activated Al, including amorphous Al, sorbed poly-nuclear hydroxyl Al, organic-bound Al, and exchangeable Al, from soil by using 0.2 mol L⁻¹ ammonium oxalate (pH = 3.0).

In a 250 mL plastic bottle, 1 g of the dried sample was mixed with 50 mL 0.2 mol L⁻¹ ammonium oxalate (pH = 3.0). The bottle was shaken for 1 h in an oscillator. The solid–liquid intermixtures was filtered, and the residue was returned to the plastic bottle. Another 50 mL of 0.2 mol L⁻¹ ammonium oxalate (pH = 3.0) was added to the plastic bottle, which was shaken for another 1 h. The solid–liquid intermixtures in the plastic bottle was filtered again, and then two filtrates were homogenized. Finally, the activated Al concentration (as Al₂O₃) in the mixed solution was determined by inductively coupled plasma–optical emission spectrometry (ICP–OES) (Thermo Fisher Scientific Inc., USA).

2.4.3. Al measurement in rice

At the harvest stage, the rice plant was divided into three parts, namely, root, stem and leaf, and grain, and then oven dried at 70 °C for 72 h. The dry weights of the three parts were determined separately. Dried tissues were finely ground in a stainless steel mill, and then subsamples were placed in 100 mL digestion tubes. A mixed acid of 10 mL of high-purity nitric acid and 5 mL of high-purity perchloric acid was added to each tube, which was left to stand overnight and then gradually heated at 140 °C to volatilize yellow brown smoke (NO₂) slowly. Next, the temperature was raised to 180 °C and held at the temperature until a substantial amount of white smoke appeared. After digestion, the solutions were cooled, diluted to 50 mL with ultrapure water (Easy-pure), and filtered into acid-washed plastic bottles. The concentrations of Al in different tissues were determined by ICP–OES (Thermo Fisher Scientific Inc., USA).

2.4.4. Cd measurement in rice

In the harvest stage, the rice plant was divided into the following five tissues: root, stem, leaf, shell, and corn. The plant materials were oven dried at 70 °C for 72 h. Then, dry weights of five tissues were separately determined. Dried tissues were finely ground in a stainless steel mill. Subsamples were placed in 100 mL Teflon tubes and digested by 5 mL of high-purity nitric acid with the CEM Microwave Sample Preparation System (Matthews, NC, USA). Next, the temperature was raised to 180 °C within 15 min and held for 15 min. After digestion was completed, the solutions were cooled, diluted to 50 mL with ultrapure water (Easy-pure), and filtered into acid-washed plastic bottles. The concentrations of Cd

<table>
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<td>First group of pot-culture experiments (g per pot; 5 kg of dried soil in each pot).</td>
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<td>Treatments</td>
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Abbreviations: DAP, diammonium phosphate; SOP, potassium sulfate; NMSC, nano-submicron mineral-based soil conditioner.

¹ For each pot, a total of 1.1 g urea was fertilized at the rice transplantation, tillering, earing, and ripening stages with the ratios 40%, 20%, 30%, and 10%, respectively.

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<td>Second group of pot-culture experiments (g per pot, 10 kg of dried soil in each pot).</td>
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Abbreviation: DAP, diammonium phosphate; SOP, potassium sulfate; NMSC, nano-submicron mineral-based soil conditioner.

¹ For each pot, a total of 2.2 g urea was fertilized in rice transplantation, tillering, earing, and ripening stages at ratios of 40%, 20%, 30%, and 10%, respectively.
in different tissues were determined with an ICP-MS 7500 (Agilent Technologies). A reagent blank and a standard reference sample (tea leaves obtained from the National Research Center for Standards, China) were used to ensure the accuracy and precision of digestion and subsequent analysis.

2.4.5. Bulk density and porosity measurement of soil

The volumetric ring method (VR) is considered a standard method for bulk density ($\rho_s$) determination. This method involves soil sampling with undisturbed structures. Therefore, the volumetric ring must be carefully removed, and the sample is not compacted. The whole ring should be filled with soil. The porosity ($t$) is calculated from the ratio between the sample dry mass (105 °C, 24 h) and the volumetric ring internal volume. The porosity can be calculated from the following equation (1):

$$p_t = (1 - \rho_s/\rho) \times 100$$

where $p_t$ is the porosity, $\rho_s$ is the bulk density, and $\rho$ is the particle density. Equation (1) indicates that the porosity and the bulk density are inversely correlated.

3. Results and discussion

In this work, the changes in pH and the accumulated effects of Al caused by NMSC, which may accumulate activated Al because it contains approximately ±5% Al_2O_3 (Table S1), were investigated by conducting pot-culture experiments with aluminum sulfate hydrate (Al(SO_4)2·18H_2O) as an added Al resource in a greenhouse in the College of Resources and Environment, China Agricultural University (Table 2). The pH and activated Al concentrations in the soil were determined (Fig. 1). pH was negatively correlated with the activated Al concentration (as Al_2O_3 g kg^-1) in the soil. With respect to the pH of the blank (Al0S0), pH decreased by 0.15 (2.65%) when 0.50 g Al was added into the soil of the pot (AI1S10). However, the pH increased by 0.39 (6.90%) and 0.28 (4.96%), when both Al and NMSC (AI1S1 and AI1S12), respectively, were added. The changes in activated Al for AI1S10, AI1S1, and AI1S12 were 5.35%, −25.73%, and −38.85%, respectively, relative to those of the blank AI0S10. As a reference of the control (AI1S10), pH increased by 8.90% and 7.17% for AI1S1 and AI1S12, respectively. The corresponding changes in Al concentration were −29.77% and −41.75%, respectively. This work shows that NMSC application improves soil pH and decreases the activated Al concentration in soil.

To confirm the function of NMSC in improving soil pH and alleviating Al toxicity, we performed another group of pot-culture tests on the soil from the same site as in the preceding experiment and similar experimental conditions (Table 3). Test data confirmed that the Al concentration decreased after NMSC was used, although the Al concentration (mg kg^-1) in different rice tissues did not exhibit a linear relationship with the increase in NMSC (T3, T4, and T5) (Fig. 2). As a reference of the control (T2), the pH increased by 0.39 (6.90%), −13.25%, and 9.51% for T3, T4, and T5, respectively. For T3, T4, and T5, the changes in the rice stem and leaf were −3.98%, −37.39%, and −13.62%, respectively, and the changes in the rice grain were −5.87%, −22.89%, and −2.64%, respectively. Given the blank (T1) as a reference, the corresponding changes were −22.04%, −27.99%, and −9.09% in the root; −44.21%, −59.64%, and −55.92% in the stem and leaf; and −6.44%, −23.52%, and −3.43% in the grain, respectively. On the basis of decreasing delivery distance, the Al concentration decreased in the following order: root, stem and leaf, and grain. The order of magnitude of the Al concentrations in the root, stem, and leaf was triple that of the concentration in the grain.

The pH, bulk density, and porosity of the soil in the second group of pot-culture tests were also determined. The results indicate that the pH was positively correlated to the dosage of NMSC used in the soil and increased with the amount of NMSC (Fig. 3). However, the bulk density and the porosity of the soil exhibited a slightly complicated variation trend with different treatments. The change in the bulk density was opposite that of the porosity based on their calculation equation. The bulk densities of the soil treated with T4 and T5 decreased relative to that of the control (T2). As a result, the porosities of the former two increased (Fig. 3).

Given the performance of NMSC in improving pH and alleviating Al toxicity, we conducted a preliminary field test in You County, Hunan Province, China (27° 0’ N, 113° 20’ E) to verify whether NMSC can alleviate Cd toxicity. The Cd concentration in the soil background was 0.3746 mg kg^-1, which indicated a slightly contaminated soil. The chosen plot was treated with the control.
and NMSC, respectively. After a two-crop (early rice and late rice) use of NMSC for the chosen plot, the soil pH and Cd concentrations of the different tissues in the late rice were determined. Compared with the control, pH was improved from 5.84 to 6.07 after fertilizing NMSC; the Cd concentrations in different tissues of the late rice were less than that of their counterparts (Fig. 4). The Cd concentrations gradually decreased in the following order: root, stem, leaf, shell, and corn in both treatments with and without NMSC. This trend was similar to that of the Al concentration in the rice as stated above, and agreed to the result reported by Xie et al. (2015). Low density is accounted for the porosity (Fig. 5). Liu et al., 2015. The hydrothermal method is the most frequently used strategy for green chemistry. Therefore, simulating the soil-forming process through the hydrothermal method is a novel concept.

First, NMSC preparation must be highlighted by the authors. By simulating soil formation, we produced NMSC from potassium-rich feldspar in an environmentally friendly hydrothermal atmosphere. In this manner, thousands of years of reaction time are reduced to a few hours or tens of hours (Table 1). A preliminary study showed that the reaction mechanism of potassium-rich feldspar under hydrothermal conditions proceeds via mineral—mineral replacement by a dissolution—precipitation process. This process is highly similar to the natural weathering of rocks (Liu et al., 2015). NMSC and soil exhibit some similar properties. The NMSC bulk density is approximately 0.75–0.85 g cm⁻³, which is attributed to porosity (Fig. 5) (Liu et al., 2015). Low density is accounted for the ability of NMSC to decrease soil bulk density (Fig. 3). Hence, NMSC may alleviate soil compaction as an important component of land degradation worldwide (Batey, 2009).

The porosity of the newly formed phases also improves the physical and chemical characteristics of soil because of their permeability and potential ability to preserve moisture and fertility. Therefore, the porosity of NMSC is very helpful for the soil. The generation of porosity during the hydrothermal reaction, as a vital feature of mineral–mineral replacement processes, has been discussed in a previous work (Liu et al., 2015). The hydrothermal method is the most frequently used strategy for green chemistry. However, simulating the soil-forming process through the hydrothermal method to amend the soil is a novel concept.

Simulating soil formation was based on the extraction of potassium from potassium-rich feldspars. Water-soluble potassium salts are abundant in few countries, such as Canada, Russia, and Belarus. By contrast, water-insoluble K resources, such as potassium feldspar, are considerably available worldwide in massive volume in the Earth's crust. K must be extracted from potassium-rich rocks to supply water-soluble K for agriculture in some
countries, such as China, Brazil, and India, with limited K salts. Studies have reported important developments in the use of potassium-rich feldspar as alternative potash in a broad spectrum of geographical contexts and soils (Liu et al., 2014; Manning, 2010). Ciceri et al. (2015) thoroughly summarized the history of potassium fertilizer development in America and Europe. In China, research on potassium extraction from rocks began in the mid-1950s, and numerous studies on the subject appeared at the beginning of the 21st century. However, no technique or method was industrialized until the 21st century because of political and economic factors, especially technical defects. Previous techniques mainly focused on extracting potassium from potassium-rich feldspars. The technique recently used by Skorina and Allanore (2014) in Massachusetts Institute of Technology is highly similar to the hydrothermal method in this study. However, Skorina and Allanore (2014) aimed to prepare potassium fertilizer from feldspars. The disadvantage of preparing potassium fertilizer from potassium-rich feldspars is the disposal of >80% solid residues in a green and low-cost manner. This disadvantage is also the main reason why no technique or method has been industrialized to date. However, simulating soil formation to utilize potassium-rich feldspars can overcome this drawback. The problem was solved because the process does not need to solely separate potassium from other elements. The preparation of NMSC does not produce any residues. The generated NMSC also effectively remediates the soil and provides nutrient elements, including K. These advantages are not offered by other techniques for the extraction of K from potassium-rich feldspars.

Second, NMSC consists of particles with sizes ranging from several nanometers to micrometers (Fig. 5). These nano-submicron particles (tens of nanometers to a few micrometers) with some clay-like properties are important in aggregate formation and directly influence the soil structure (Bronick and Lal, 2005). In nature, minerals are more complex than previously thought because their chemical properties vary as a function of particle size. This relation is observed when the particles are smaller than a few nanometers to as much as several tens of nanometers. These variations may produce differences in important geochemical and biogeochemical reactions and kinetics (Hochella et al., 2008). Lombi et al. (2003) reported that conditioners with colloids of <0.2 μm diameter significantly decrease the lability of Cd, Zn, and Cu in soil samples and conditioners become resistant to heavy metal lability even when soils are reacidified. Lombi et al. (2003) concluded that a combination of pH-dependent and pH-independent mechanisms may be responsible for the observed metal fixation. The available information in this paper definitely supports this conclusion.

Third, NMSC is a slow-release nutrient reserve. Approximately 80% of the available potassium is water soluble. Other elements, including some secondary and minor elements for plants, are also soluble. Fig. 6 shows that the morphology substantially changes when NMSC is leached by deionized water and 0.5 mol L⁻¹ HCl. This result agrees with the X-ray powder diffraction (XRPD) analysis (Fig. S1). The XRPD results confirm that only butschliite was dissolved in deionized water (almost unchanged in Fig. 6A). By contrast, all phases except potassium feldspar (residue in Fig. 6B) were dissolved in 0.5 mol L⁻¹ HCl. In addition to the major elements N, P, and K, some secondary and trace elements called micronutrients, including Si, Ca, magnesium (Mg), S, copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), Mo, and B, are essential to plant growth (Asher, 1991; Epstein, 1999; He et al., 2005; Welch, 1995). Most of these secondary and trace elements are available in NMSC. The slow release of nutrients helps improve the fertilizer efficiency and benefits agriculture, environment, and economy (Chien et al., 2009). Trace elements are also critical for crop breeding with micronutrients to protect humans from micronutrient deficiencies (Welch and Graham, 2004). The “law of the minimum” presented by Liebig states that plant growth is limited by a single resource at any one time. Despite the law’s controversy (Rastetter and Shaver, 2006).
1992; Rubio et al., 2003), it is a universal phenomenon that explains the deficiencies in some micronutrient elements (Cakmak, 2002; Jones et al., 2013), especially in some developing countries, including China (Yang et al., 2007). As a pool of multiple elements, NMSC will supply some of the necessary micronutrients to people through the food chain.

Fourth, NMSC is composed of minerals that can buffer soil acidification and alleviate metal element toxicity. For example, NMSC consists of tobermorite, hibschite, butschliite, calcite, and unreacted potassium feldspar when produced from the hydrothermal reaction between potassium feldspar and lime under 190 °C for 10 h. The butschliite (K₂Ca(CO₃)₂) and calcite (CaCO₃) can react with H⁺ in the soil to improve the soil pH (Figs. 1 and 3). Al exists in the hibschite phase and can only be dissolved in 0.5 mol L⁻¹ HCl. The release rate from the soil is extremely slow. Previous research confirmed that some healthy elements, such as Si and Ca, can compete with unhealthy elements and alleviate the stress induced by unhealthy elements. Examples of such phenomenon include the Si-induced (Kidder et al., 2001; Wang et al., 2004) or Ca-induced (Rengel, 1992; Rengel and Zhang, 2003) amelioration of Al toxicity and the Si-mediated (Adrees et al., 2015; Kirkham, 2006; Shi et al., 2005) or Ca-mediated (Wang et al., 2015a) inhibition of Cd absorption. These occurrences are possible except when the increase in pH alleviates Al toxicity and inhibits Cd absorption. However, no direct evidence supports the assumption that the competitive absorption of nutrient elements is the cause of the decreasing Al and Cd concentrations. Cd sorption and desorption in soils are also affected by several factors (Loganathan et al., 2012; Shaheen et al., 2013). A preliminary test showed that available K, Si, and Ca increased in the soil. Likewise, organic matter in a continuous field test also increased when a similar program was carried out in the same location in spring in 2015 (Fig. 52). Further analysis showed that Cd content in the rice further decreased from 0.08 mg kg⁻¹ to 0.04 mg kg⁻¹. At two times decrease in Cd content was again replicated.

As a layered silicate, tobermorite exhibits high exchangeability and selectivity for cations (Komarneni and Roy, 1983). This attribute can alleviate the damage of heavy metals, such as Cd, Pb, and Cr, on soil (Coleman, 2006; Pena et al., 2006). Tobermorite is also a slow-release reservoir for some nutrients, such as [K⁺] and [NH₄⁺] (Yao et al., 1999). As a primary product of NMSC, tobermorite can reach a weight percentage of 40% when reaction conditions are controlled (Liu et al., 2015). Tobermorite possesses a structure similar to that of the 2:1 clay minerals. This structure is implicated in soil K cycle (Hinsinger, 2002) and is positively correlated with pH buffering capacity (Weaver et al., 2004; Xu et al., 2012). As such, this structure facilitates the maintenance of an ecological balance.

4. Conclusions

In summary, NMSC was prepared through an environmentally friendly method and comprehensively analyzed (Supplementary Material). The good performance of the proposed NMSC is closely related to its physicochemical characteristics because of multifactor synergy. Although hydrothermal method is the most frequently used approach, NMSC preparation through rock weathering simulation is a novel concept, which differs from traditional chemical practices in agriculture. This approach can be employed to form new products with similar physicochemical properties to soil and provides products with various functions and characteristics. The proposed simulation technique can be used as a basis for new agricultural revolution. Hence, common perceptions on soil fertilization through environmentally friendly mechanisms can be altered, and the soil and the environment are positively affected.

Acknowledgments

This research project was supported by Projects in the National Science and Technology Pillar Program during the Eleventh Five-Year Plan Period (China; Grant No. 2006BAD10B04) and the Knowledge Innovation Project of the Chinese Academy of Sciences and Spark Program of China (Grant No. 2007EA173003). Two anonymous reviewers are thanked for their constructive critical suggestions aimed to improve the quality of the manuscript. Additionally, the critical comments of the editors also helped to improve the paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2017.02.155.

References


