Research Article

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A mechanochemical preparation, properties and kinetic study of kaolin–N, P fertilizers for agricultural applications**

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Abstract: Solvent-free ball milling was used to activate kaolin, a trioctahedral clay material, with diammonium phosphate[(NH₄)₂HPO₄] to serve as a fast-acting phosphorus and nitrogen releasing fertilizer. Different tests on a mixture of 3:1 weight ratio of kaolin: (NH₄)₂HPO₄ were performed to analyze the level of incorporation of (NH₄)₂HPO₄ in the kaolin and the degree of liberation of NH₄⁺ and PO₄³⁻ ions into solution. The experimental mill speeds were varied from 200 to 700 rpm rotational rates for a fixed period of 2 hours. Several milling periods of 1, 2, and 3 h. were studied at the fixed milling speed of 600 rpm. To explain the properties of activated materials and to understand the purpose behind the simpler disintegration of phosphorus, several analytical methods such as FT-IR, TGA-DTG and Ion chromatography (IC) were used. The proposed procedure was environmentally friendly, and it helped to maintain a balanced supply of nitrogen and phosphorus fertilizer for agriculture's long-term development by offsetting some of the existing high-cost chemical fertilizer. The results demonstrated that the mechanochemical reaction could yield an intercalated form of kaolin that is a transmitter of N and P sources in fertilizers.

Keywords: Solid-state, high energy ball milling, sustainable slow-release fertilizers, diammonium phosphate

1 Introduction

Most manufactured fertilizers contain N, P, and K compounds that are highly soluble and volatile which makes them susceptible to environmental loss into the surrounding soil that, in turn, increases soil and water pollution [1]. This loss can lead to the increased usage of fertilizers in order to fulfill a sustainable and sufficient food production which means more pollution and more cost. Furthermore, the lack of NPK resources may undermine food security and requires changing the way to deal with fertilizer management [2].

Inorganic fertilizers are the most common type in the agricultural chemical industry. Generally, fertilizers should boost plant development by delivering the needed nutrients to crops. They also play a vital role in controlling the pH and fertility of the soil. Mineral fertilizers production has increased over the years in parallel with the rise of human population and their need for food [3, 4]. In this regard, it is known that the main nutrients for plant growth are nitrogen, phosphorus, and potassium [5]. Usually, phosphorus is recovered from different types of clay minerals such as kaolin and feldspar, which are abundant in the soil, but quite imbalanced in their allocation.

Solid-state mechanochemical processes are regarded as a long-term free-solvent material synthesis approach [2, 6, 7]. Co-grinding clay minerals like talc and kaolin with chemical salts of N, P, and K as source ingredients could result in extremely efficient slow-release fertilizers [7–9].

According to previous research results, the solid-state mechanochemical reactions to prepare slow-release fertilizers (SRF) can be achieved by the ball milling of kaolin or Al₂O₃ with soluble salts of N, P and K [10–12].

Al-Rawajfeh *et al.* [13] used a planetary ball mill to crush various mixtures of kaolin with KH₂PO₄ or (NH₄)₂HPO₄. To investigate the intercalation of KH₂PO₄ and (NH₄)₂HPO₄ into kaolin layers to release K⁺, NH₄⁺ and PO₄³⁻ ions into solution, various samples containing 25 to 75wt.% kaolin were milled at 600 rpm for 2 hours. Their findings revealed that the mechanochemical approach can

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be used to create crystalline kaolin that can be employed as a barrier layer for the controlled release of nutrients including K^+ , PO_4^{3-} and NH_4^+ as fertilizer.

Even though solubilization and release of compound species are basic physico-chemical processes with a range of applications [14], the examination of release kinetics and mechanisms is of enormous importance for the deep understanding of the behavior of SRFs, mechanisms and kinetic processes for drug administration and formulation have been reported in various research [15]. Natural and/or manufactured chemicals have been employed for the release of plant nutrients, moreover, corrosion behavior study of galvanized steel in seawater environment and for solar panels [16, 17].

The current research aims to investigate the effects of milling speed and time on the characteristics of the (kaolin– $(NH_4)_2HPO_4$) system, to reduce the kaolin clay mineral to an amorphous phase and develop a novel chemical bonding as an amorphous phase between K–Al–Si–P–O. The one-of-a-kind target product will eventually deliver a moisture layer structure SRFs that limit NH_4^+ and PO_4^{3-} nutrient release into the soil.

2 Experimental

2.1 Materials and mechanochemical process

Diammonium phosphate $[(NH_4)_2HPO_4]$ was purchased from Panreac, Spain (> 90%). Kaolin $(Al_2Si_2O_5(OH)_4)$ was collected from Wadi Araba region, south of Jordan [18, 19]. A planetary Fritsch Pulverisette-7 ball mill (Germany) that has two zirconium milling jars (45 cm^3 interior volume each) with six zirconium balls of 15 mm diameter was used for the milling process that is considered as solvent-free. Table 1 shows the experimental conditions involved in the experiments (ratio, milling speed and duration).

Table 1: The experimental mixture ratios and conditions.

Series	Sample (Kaolin: $(NH_4)_2HPO_4$) weight ratio	Milling speed (rpm)	Duration (min)
Exp. 1	3:1	200, 400, 600 700	120
Exp. 2	3:1	600	60, 120, 180

To avoid excessive heat that might affect the results of the milling process, the experiments were run for 10-minute periods separated by a 5-minute rest time.

2.2 Characterization

The morphology change of the produced samples was followed by using a Fourier transform infrared spectrometer (FTIR, NEXUS, EPS-870) in the wavenumber range of 4000 to 500 cm^{-1} with 2 cm^{-1} resolution. Thermogravimetric analysis (TGA) curves were obtained with a (TG-DTA, STA-409 PC, NETZSCH) at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1000°C in an N_2 atmosphere.

To study the kinetics of leaching experiments of the mechanically activated kaolin– $(NH_4)_2HPO_4$ to release nutrients, the milled materials were disseminated in an aqueous solution (1 g milled sample, 50 mL distilled water) in a 100-mL glass beaker at room temperature for 1 day, 2 days, and 7 days. After leaching, a filter paper with a pore size of 0.45 m was used to carry out the suction filtration for the solid–liquid separation. The quantities of NH_4^+ and PO_4^{3-} nutrients released in the filtrate were determined using ion chromatography (IC, column series Dionex, CS-5000+DP, Germany).

3 Results and discussion

The first part deals with the results of varying the milling speed for the (3:1) kaolin– $(NH_4)_2HPO_4$ mixture while the second part shows results of changing the milling duration. Finally, the kinetics study results of ammonium and phosphate ions leaching are presented.

3.1 Effect of milling speed

Figure 1 shows the XRD patterns of kaolin– $(NH_4)_2HPO_4$ (3:1) mixture as well as their corresponding starting materials milled at a speed of 600 rpm for 120 min. The XRD patterns showed that some characteristic patterns corresponding to $(NH_4)_2HPO_4$ and kaolin had disappeared in the milled product, which clearly suggests that $(NH_4)_2HPO_4$ gets incorporated into the amorphous structure of kaolin [13].

According to the FTIR results, dihydroxylation of the silicate layers occurs after physio-chemical treatment of kaolin clay minerals with $(NH_4)_2HPO_4$, as shown in Figure 2. The stretching vibrations of the hydroxyl groups at 3688 and 3619 cm^{-1} diminish with increasing milling speed

Figure 1: XRD patterns of kaolin–(NH₄)₂HPO₄ sample system milled at speed 600 rpm for 120 min [13]

Figure 2: FTIR spectra of kaolin–(NH₄)₂HPO₄ samples milled at different milling speed for 120 min

and disappear for samples prepared at 700 rpm, according to the spectra of kaolin–(NH₄)₂HPO₄ sample mixes.

Untreated kaolin samples can be classified into one of two types of hydroxyl groups. The inner hydroxyl group resides within lamellae in plane common to both the tetrahedral and octahedral sheets at 3684 cm⁻¹, and inner hy-

droxyl group lie within lamellae in a plane common to both the tetrahedral and octahedral sheets at 3627 cm⁻¹. The intensity and position of inner surface hydroxyl groups are generally changed by intercalation; however, intercalation did not influence on the band at 3619 cm⁻¹ [20, 21]. As can be shown in this study, kaolin clay material has four dis-

tinct IR bands, whereas badly organized kaolin only has three [22]. The Si-O stretching area consists of stretching bands at 1113, 1000-1003, and 1030 cm^{-1} , as well as Si-O bending vibrations at 790, 751 cm^{-1} , and 688 cm^{-1} . The inner hydroxyls are ascribed to the Al-OH bending vibration at 912 cm^{-1} . The sample also shows the vibration of the inner surface hydroxyl groups at 936 cm^{-1} [22, 23].

The hydroxyl vibration disappearance at 912 cm^{-1} and the intensity decreases of the Si-O band at $\sim 1000 \text{ cm}^{-1}$ that confirm the mechanochemical decomposition of kaolin at 700 rpm. Solihin, *et al.*, [8] study illustrated a milling process for kaolin-sample mixtures at a minimum of 400 rpm milling speed is required to intercalate nutrients such as $(\text{NH}_4)_2\text{HPO}_4$ into the amorphous kaolin structure. However, at mill speeds above 400 rpm, the beginning samples were gradually reduced to an amorphous state at mill speeds above 400 rpm, which could indicate that $(\text{NH}_4)_2\text{HPO}_4$ has been integrated into the amorphous structure of kaolin, which has already been proven by XRD [8].

The FTIR spectra shown in Figure 2 elucidated that at lower milling speeds, below 400 rpm, characteristic spectra corresponding to residual raw materials exist in the products, like as a distinct kaolin peak from 3627-3685 cm^{-1} . Moreover, the disappearance of the preceding peaks at milling speed above 400 rpm pointed to reducing the starting samples into an amorphous state, which might suggest that $(\text{NH}_4)_2\text{HPO}_4$ has been intercalated into an amorphous kaolin [7].

Also, the broad N-H bands located between 2700-3200 cm^{-1} was disappeared after samples milling, illustrated the formation of new product kaolin- $(\text{NH}_4)_2\text{HPO}_4$ system.

The distinctive band of the Si-O, which stretches approximately 1049 cm^{-1} for high milling speed samples, increased broader and shifted for milled samples to a higher frequency, as evidenced by the development of amorphous silica during the mechanochemical reaction.

Figure 3 demonstrates that the observed mass loss of 12.3% caused by thermal dehydroxylation of the kaolin in the temperature range of 450 to 650°C agrees well with the predicted value of 13.96%, indicating that the starting kaolin is of good purity. The ammonium monohydrogen phosphate salts disintegrate in essentially two phases, exhibiting endothermic peaks for ammonium monophosphate at 187°C and 600°C, respectively, whereas, decomposing into two steps for sample milled at 200 rpm with peaks at 185°C and 580°C (Figure 3), which illustrate that some of the starting materials have remained. However, decomposing into one step for sample milled at 700 rpm at 100°C is relating to water transfer, these findings revealed that solid-state mechanochemical treatment resulted in increased water sorption due to crystal size reduction. It

should also be noted that, unlike the precursors, the thermal decomposition of kaolin/ K_2HPO_4 was not a multi-step process, but rather a sluggish continuous process that terminated approximately 650°C. [9].

Figure 3: TGA patterns of kaolin- $(\text{NH}_4)_2\text{HPO}_4$ sample mixture milled for 120 min at different milling speeds

Table 2 shows the release of NH_4^+ and PO_4^{3-} components from kaolin- $(\text{NH}_4)_2\text{HPO}_4$ combinations milled at various milling speeds and dispersed in distilled water for 24 hours and illustrated that the nutrients concentrations are decreased as milling speeds increased.

Table 2: Concentration in (ppm) of NH_4^+ and PO_4^{3-} nutrients released from kaolin- $(\text{NH}_4)_2\text{HPO}_4$ samples milled at different milling speed for 2 h

Milling Speed (rpm)	Conc. of NH_4^+ (ppm)	Conc. of PO_4^{3-} (ppm)
200	6122.5	3456.6
400	4246.7	2553.0
600	303.2	415.1
700	99.9	88.3
St.Dev	2978.297	1637.193

The NH_4^+ and PO_4^{3-} ions are highly soluble in water for samples milled at 200 rpm, but the easily soluble $(\text{NH}_4)_2\text{HPO}_4$ patterns remained in the milled samples, indicating that the nutrients had not yet been absorbed into the kaolin structure. However, Figure 4 shows that samples processed at 400 rpm released significantly fewer nutrients. This result is consistent with findings from FT-IR and TGA (Figures 1 and 2, respectively). Complete amorphization was found in sample combinations milled at 600 rpm and above, and the subsequent release of nutrients declined, reaching an average of roughly 100 ppm after 24 hours of leaching. To decrease $(\text{NH}_4)_2\text{HPO}_4$ to the amorphous phase and allow nutrients to be incorporated into the kaolin structure, higher mill rotational speeds were necessary. Figure 4 depicts the nutrients release behavior of

Figure 4: Profile of nutrients release of kaolin–(NH₄)₂HPO₄ sample mixtures milled for 2 h at different milling speeds and dispersed in distilled water for 24h

(kaolin–(NH₄)₂HPO₄ samples when distributed in water for 24 hours as a function of mill rotational speeds.

3.2 Milling time effect

At three milling times of 60, 120, and 180 minutes, the impact of milling time on the 3:1 weight ratio characteristics of kaolin–(NH₄)₂HPO₄ mixture milled at 700 rpm was examined. FT-IR spectra of kaolin–(NH₄)₂HPO₄ samples with a ratio 3:1 that milled at the speed of 700 rpm for several different durations discussed in [13].

The band vibration intensities fluctuated as the milling time increased, especially at a peak of about 915 cm^{−1}. Also, on the different milling samples, the kaolin peaks with strong absorption intensity, at 3620–3690 cm^{−1}, could not be seen, showing that intercalation occurs. The intensity of the peaks diminished as the time approached 180 minutes. However, the disappearance of peaks detected at 915 cm^{−1}, 3627, and 3684 cm^{−1} for samples with milling time above 120 min indicated that the raw materials were reduced to an amorphous form, suggesting that (NH₄)₂HPO₄ has been absorbed into the amorphous structure of kaolin.

Figure 5 represents thermal gravimetrical patterns for kaolin–(NH₄)₂HPO₄ samples milled at 700 rpm for different duration and shows that no distinguished mass-loss features were reported for the starting materials at any milled time, which attests to their destruction during grinding indicated that 60, 120 and 180 min are suitable periods for preparing slow released fertilizer from kaolin–(NH₄)₂HPO₄.

Table 3 summarizes the concentration of nitrogen and phosphorus nutrients with milling time released from kaolin–(NH₄)₂HPO₄ that were milled at 700 rpm for different milling times.

Figure 5: TGA patterns of kaolin–(NH₄) samples milled at 700 rpm for different duration

Table 3: Concentration of NH₄⁺ and PO₄^{3−} nutrients in (ppm) released from kaolin–(NH₄)₂HPO₄ samples milled at 700 rpm for various milling time

Milling Time (min)	Conc. of NH ₄ ⁺ (ppm)	Conc. of PO ₄ ^{3−} (ppm)
60	372.5	767.0
120	303.0	415.1
180	37.0	48.4

Figure 6: Nutrients release profile of kaolin–(NH₄)₂HPO₄ milled at 700 rpm at varying milling time and disseminated in distilled water for 24h

The release of NH₄⁺ and PO₄^{3−} nutrients into solution was 372.5 and 767.0 ppm for sample mixes prepared in 60 minutes, however, when milling time was prolonged from 60 to 120 minutes, the release of NH₄⁺ and PO₄^{3−} nutrients into solution was dramatically reduced, reaching 303.0 and 415.1 ppm respectively, also another distinctive decreased 37.0 and 48.4 ppm respectively, for samples prepared at 180 min as milling time, referring that sufficient milling time was required to complete intercalation of (NH₄)₂HPO₄ into an amorphous structure of kaolin.

The nutrients profile of NH₄⁺ and PO₄^{3−} ions released from kaolin–(NH₄)₂HPO₄ samples milled for different

milling time and dispersed in water for 24 h shown in Figure 6.

3.3 Kinetics results

The nutrient release kinetics were determined in this study using a quantitative examination of the concentration of phosphorous in solution throughout time. Figure 7 shows the concentration of phosphate ion for the system milled at 700 rpm for 2 h.

Figure 7: Release of phosphate ion from the kaolin– $(\text{NH}_4)_2\text{HPO}_4$ system milled at 700 rpm for 2 h

For the kaolin– $(\text{NH}_4)_2\text{HPO}_4$ system, the concentration changes of PO_4^{3-} released increases with time. Since $(\text{NH}_4)_2\text{HPO}_4$ was used for P loading, even though the rate of increase was noticeably slower, the concentration of P increased over the duration of the experiment (168 hours, or 7 days). In the leaching solution, the total released amount of PO_4^{3-} reached a value of 102.4 ppm in the first 48 hours, which represents around 16% of the initial concentration of the total released amount of PO_4^{3-} while the amount increased to 142.6 ppm (61.5% of the initial concentration) after 168 hours. This is an excellent representation of a slow-release fertilizer model.

4 Conclusions

A solid-state mechanochemical method was used to synthesize slow-release N and P fertilizer ingredients using kaolin as the host material and $(\text{NH}_4)_2\text{HPO}_4$ as the precursor. Only the conversion of diverse N, P sources in solid clay minerals was possible using the free-solvent procedure via milling. The adopted process was both environmentally friendly and economically feasible for supplying an alternative to the current chemical fertilizer, which is typically obtained

from some salt-water lakes, and it is expected to make a significant contribution to the balanced development of N and P fertilizers. The slow-release characteristic behavior for phosphorous was evidenced through a kinetics study.

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