

Solid-state mechanochemical activation of clay minerals and soluble phosphate mixtures to obtain slow-release fertilizers

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ABSTRACT: This work describes the development of potential multi-element slow-release fertilizers obtained by mechanochemical activation of mixtures of kaolinite and ammonium or potassium monohydrogen phosphates. Preliminary results of talc amorphization have also been included. The methodology consists of milling the materials in a high-energy ball mill, where the influence of rotation and time of milling were investigated. The samples were characterized by XRD, FTIR, TGA/DTA, SEM and MAS-NMR. The experimental results explain the slow-release behaviour of the amorphous nanostructured materials in aqueous suspensions, especially the MAS-NMR spectra, which showed the changes in the chemical environment of the elements analysed. The materials displayed slow-release behaviour for phosphates probably because the aluminium ions in the mineral structure interact more thoroughly with phosphate than potassium or ammonium. Nevertheless, in general, all of the nutrients were released slowly.

KEYWORDS: Mechanochemical activation, mineral fertilizers, clay mineral, macronutrients.

The development of slow-release fertilizers is based on the need to improve the performance of conventional fertilizers (Wu *et al.*, 2008) and minimize socio-environmental problems by reducing pollution caused by the excess nutrients used in agriculture (Li & Zhang, 1999). Slow-release fertilizers also enhance the production of food and prevent damage from the potential loss of conventional compound-mineral fertilizers through leaching and volatilization (Shaviv, 2001; Tong *et al.*, 2009).

Mechanochemical activation of layered minerals, especially clay minerals, has been studied exten-

sively in the past and the observed effects include: increase of defects in the materials, increases in the chemical reactivity and solubility of the minerals, reduction of thermal stability and mechanochemical intercalation (Mingelgrin *et al.*, 1978; Garcia *et al.*, 1991; Aglietti *et al.*, 1994; Yariv & Lapidés, 2000; Mendelovici, 2001; Frost *et al.*, 2001, 2003; Petrovic *et al.*, 2002; Hrachová *et al.*, 2007; Vizcayno *et al.*, 2010; Sun *et al.*, 2011; Makó *et al.*, 2014). Recently these processes were used in the synthesis of potential slow-release fertilizers, where soluble phosphates were mixed with alumina (Al₂O₃) (Zhang *et al.*, 2009), magnesium hydroxide (Solihin *et al.*, 2010) and, more recently, clay minerals from the kaolin group (Solihin *et al.*, 2011).

In the case of clay minerals, the process consists of grinding the material with a conventional,

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usually highly soluble, fertilizer to obtain nano-structured metastable phases that provide slow release of nutrients. The delay in the availability of nutrients for plant uptake and use after application and/or extension of their availability in the soil is the main characteristic of this type of fertilizer (Bhardwaj *et al.*, 2012).

In this study, the clay mineral kaolinite, which is very common in Brazilian soils, was used. Grinding produces highly reactive amorphous nanostructured materials that are capable of reacting with soluble fertilizers such as ammonium or potassium phosphate and, consequently, these materials can retain elements like potassium and delay their release, for example, into water (McDowell & Sharpley, 2001). Kaolinite has a layered structure, composed of octahedral alumina and tetrahedral silica sheets (Wypych, 2004), thus, it is possible to promote the amorphization of kaolinite by grinding, especially when shear forces are used.

Thus, this research aimed to produce potential slow-release fertilizers with nitrogen, phosphorus and potassium by mechanochemical reactions between kaolinite and ammonium monohydrogen phosphate or potassium monohydrogen phosphate.

MATERIALS AND METHODS

Mechanochemical reactions between high-purity kaolinite from Rio Capim, PA, Brazil ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) (Lombardi *et al.*, 2002; Schreiner *et al.*, 2002) and ammonium monohydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) Merck, P.A. (sample KAP) or potassium monohydrogen phosphate (K_2HPO_4) Merck, P.A. (sample KKP), were performed with a Fritsch high-energy ball mill (Pulverisette 5 model). During grinding, one steel vessel of 250 mL was used, containing 15 steel balls 10 mm in diameter and a 1:1 mass ratio of kaolinite to phosphate, for each mixture (~6 g).

All reagents and samples were characterized by X-ray powder diffraction (XRD), using a Shimadzu XRD-6000 diffractometer. Fourier transform infrared (FTIR) spectra were obtained in transmission mode in a Bio-Rad FTS 3500GX apparatus, using KBr pellets, with accumulation of 32 scans from 400 to 4000 cm^{-1} and resolution of 4 cm^{-1} . Thermal analysis (simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) was performed with a Mettler Toledo TG/DTA-s 851 E thermal analyser. The samples and reagents were analysed by scanning electron

microscopy (SEM) using a JEOL JSM-6360LV microscope, with an accelerating voltage of 15 kV. Solid-state nuclear magnetic resonance (MAS-NMR) spectra were obtained with a Bruker Avance III 400 spectrometer operating at a field of 9.4 T using a Bruker CPMAS probe, a 4 mm rotor with a sample spinning frequency of 12 kHz.

To verify the release of nutrients (N, P and K), 50 mg of each sample was immersed in 10 mL of bi-distilled water at ~25°C for various times (6 to 72 h). Colorimetric analysis with indophenol blue was used to determine the nitrogen content of the filtered solution (Searcy *et al.*, 1967; Patton & Crouch, 1977; Harfmann & Crouch, 1989). The phosphorus content was measured by the molybdenum blue method (Galhardo & Masini, 2000) and the potassium content was determined by flame photometry (Holler *et al.*, 2009).

RESULTS AND DISCUSSION

In the high-energy ball-mill it was possible to investigate the influence of the speed and time of milling. For this reason, a series of experiments was performed which involved the milling of kaolinite and potassium monohydrogen phosphate to establish processing conditions that maximize the slow-release behaviour of nutrients, according to a 2² factorial design (Table 1). In the present case, phosphorus was used to monitor the release behaviour after the samples had been placed in water for 6 h.

For the samples milled in the high-energy ball-mill, beginning with experiment 3 (sample e3), the characteristic diffraction peaks of both the kaolinite (Hongbin, 2010) and the salts disappeared. Broad diffraction bands (humps) typical of amorphous materials appeared, indicating amorphization of the materials (Fig. 1).

Amorphization was also observed for samples subjected to longer rotation times (e3 and e4) and for intermediate rotation and milling times (e5, e6 and e7). For samples milled at low rotation (e1 and e2), there was partial preservation of the kaolinite structure, while in all experiments the diffraction maxima of the salts were not preserved. The XRD patterns showed that the time variable was not significant.

Having a neutral layered structure, the kaolinite does not tend to react with other compounds, such as the phosphate salts of interest to this study; however, the formation of an amorphous material

TABLE 1. Experimental design 2² for the high-energy planetary mill.

Variables	Rotation (g / rpm) Time (h)	Level (-)	Level (0)	Level (+)
		0.419 / 100 1	2.620 / 250 2	6.708 / 400 3
Code	Variables	P release (%) from KKP		
e1	-	-	95.39	
e2	+	-	93.49	
e3	-	+	37.62	
e4	+	+	21.01	
e5	0	0	77.71	
e6	0	0	76.19	
e7	0	0	76.14	

enhanced interactions with the salts and modified the solubility profile of the compounds produced.

The XRD results (Fig. 1) and the FTIR spectra (Fig. 2) indicate that chemical reactions did not occur at low rotation in the high-energy ball-mill (e1 and e2). The spectra of these samples show only an overlap relating to the physical mixture of the reactants.

The samples e3–e7 showed that the mechanochemical amorphization was related to the dehydroxylation of the kaolinite, as the typical bands of the inner surface hydroxyls (3700–3652 cm⁻¹) and internal octahedral layer hydroxyls (3620 cm⁻¹) had

disappeared. According to the generally accepted concept of mechanochemical dehydroxylation (Miller & Oulton, 1970; Yariv & Shoval, 1975; Kristof *et al.*, 1993; Frost *et al.*, 2001), these hydroxyl groups form coordinated water molecules by proton transfer. Furthermore, in the region around 1000 cm⁻¹, distinct broad bands were observed for all samples, due to the overlap of the vibrations of the Al–OH, Si–O and P–O groups (Fukamachi *et al.*, 2007).

The samples e5, e6 and e7 (milled at 2.620 g) show that rotation speed has a significant effect on the dehydroxylation process and consequently the

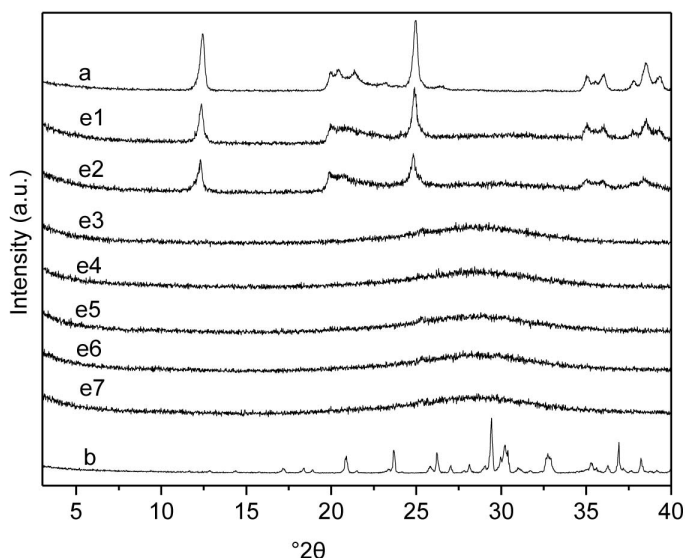


FIG. 1. X-ray diffraction patterns of the KKP samples milled according to the factorial design of Table 1: (a) = kaolinite and (b) = potassium monohydrogen phosphate.

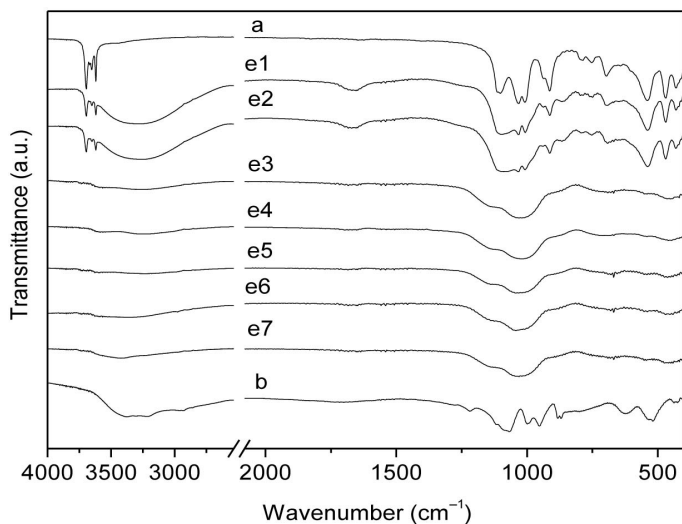


FIG. 2. FTIR spectra of the KKP samples milled according to the experimental design of Table 1: (a) = raw kaolinite and (b) = potassium monohydrogen phosphate.

mechanochemical reaction. After mechanochemical dehydroxylation, the amorphous structures that are derived from kaolinite establish weak bonds with the cations and anions from the phosphate salts and thus release their nutrients slowly. Even if practically insoluble silicon and aluminium phosphates are formed, they do form metastable nanostructures that allow these elements to be

leached out into water, which in turn allows their use in agriculture.

In order to demonstrate the influence of the high-energy ball-milling process and to verify those variables controlling the amorphization process, statistical analysis with the *Statistica*[®] v.8.0.360 software was performed using the factorial design approach. From the Pareto chart (Fig. 3) for the

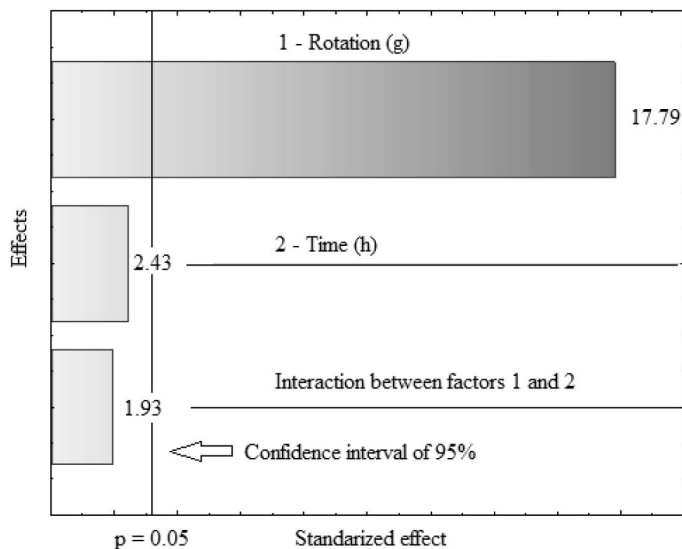


FIG. 3. Pareto chart showing the main factors contributing to phosphorus release.

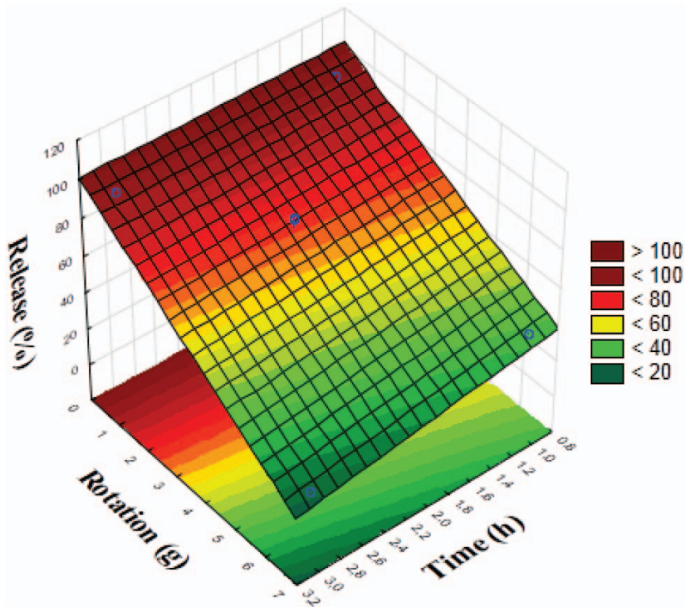


FIG. 4. The influence of mill rotation rate and milling time on the release time of phosphorus from KKP.

interaction between the factors: time, rotation and combined factors, at 95% confidence, it was considered that the major contributing factor to the delayed release of phosphorus is the rate of mill rotation (considering the estimated absolute value of 17.79 of the standardized effect), followed by the grinding time (2.43) and the combination of the two factors (1.93).

However, for these last two factors, the influence was not significant. A surface chart was generated (Fig. 4) to show the interaction of the factors that influence the delayed release of phosphorus. This chart is useful from an empirical point of view as it

indicates an association between phosphate release and the milling parameters. It can also be used to compare the theoretical and empirical models. Using the analysis of variance (ANOVA) (Table 2) and analysing the tabulated values of F_{tab} and F , specifically, it is obvious that these two factors and their combination are important in the process of delaying the release of nutrients, as the F values are greater than the values of F_{tab} .

The sum of square (SQ) values in Table 2 suggest that the model developed is suitable for explaining the observed phenomena as it presents an error of only 43.26 against a total of

TABLE 2. Analysis of variance (ANOVA) for the experimental data for phosphorous release from KKP.

SOURCE	SQ	DF	QA	F	F_{tab}
(1) Time	85.655	1	85.655	5.9268	0.092956
(2) Rotation	4575.126	1	4575.126	316.5698	0.000387
(1) by (2)	54.096	1	54.096	3.7431	0.148479
Error	43.357	3	14.452	—	—
Total	4758.233	6	—	—	—
R^2	0.99	—	—	—	—

SQ (sum quadratic), DF (system degree of freedom), QA (quadratic average), F (statistical rejection factor calculated from the QA and its residue) and F_{tab} (tabulated F factor).

4758.23 (0.91%). Moreover, the SQ values and the comparison of F with F_{tab} , indicate that factor (2) – rotation – has the greater influence on the slow-release behaviour (F_{tab} smaller than 0.05).

The graph of the results predicted by the model generated from the experimental and observed data presented an excellent linear correlation of points (data not shown).

Based on the preliminary results on release of nutrients and the statistical treatment that was performed for the milled mixture of kaolinite and potassium monohydrogen phosphate in the high-energy ball mill, samples KAP (kaolinite with ammonium phosphate) and KKP (kaolinite with potassium phosphate) were ground at a milling rotation of 6.708 g (400 rpm) for 3 h and these samples were used to investigate systematically the release process of nutrients into water. The samples produced characteristic amorphous structures, as evidenced by the humps at 25–35°2 θ , similar to the samples described in Fig. 1. Moreover, the IR spectra of the samples KKP (Fig. 2) and KAP (not shown) were very different from those of the original reactants: the mechanochemical dehydroxylation being evidenced by the absence of internal and external hydroxyl bands of kaolinite in the milled material.

SEM observations (data not shown) showed the presence of pseudo-hexagonal platelets, typical of the kaolinite structure. Both the ammonium and potassium monohydrogen phosphates presented well-defined compact crystals, as expected for materials obtained by evaporation of their solutions on an aluminium sample holder. After grinding, the well defined morphology disappeared, forming a

compact mixture without apparent structural organization and with significantly reduced particle size, in accordance with the XRD and FTIR results.

The measured mass loss of 14.7%, due to the thermal dehydroxylation of the kaolinite (Fig. 5A-a), is in good agreement with the expected value of 13.96%, thus proving the good purity of the kaolinite used. The phosphate salts decompose in basically two steps, with endothermic peaks at 230°C, 673°C and 770°C for potassium monohydrogen phosphate and 68, 145 and 426°C for ammonium monohydrogen phosphate (Fig. 5B-d,e).

The mass-loss characteristics of the starting materials were not observed in the milled samples KAP and KKP, which attests to their destruction during grinding; only one mass-loss event, attributed to the elimination of physically adsorbed water, was observed at ~115–120°C (Fig. 5-b,c). Although the water content in the sample KAP was different from that in sample KKP (27.5% and 11.4%, respectively), the observed behaviour was in agreement with other instrumental techniques, which showed the formation of amorphous phases derived from the mixture of the reagents.

The ^{27}Al MAS-NMR spectrum of the kaolinite (Fig. 6A-c) showed octahedral aluminium sites at $\delta = 1.60$ ppm (Fernandez *et al.*, 2011). However, the KKP sample (Fig. 6A-b) showed two peaks. The first peak at $\delta = -5.56$ ppm (10.7% of the Al sites), was attributed to octahedral sites that had been modified by the adsorption of the phosphate fertilizer to give an amorphous aluminosilicate, together with $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$ species (Lookman *et al.*, 1977). The second peak at $\delta = 49.45$ ppm (82.3% of the Al sites), was attributed to tetrahedral

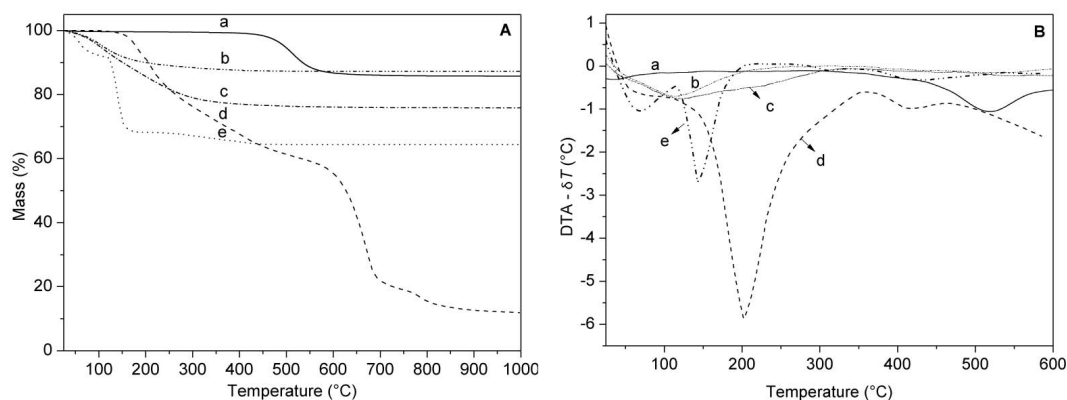


FIG. 5. TGA (A) and DTA (B) curves from the starting materials ((a) kaolinite, (d) ammonium monohydrogen phosphate and (e) potassium monohydrogen phosphate) and the samples ((b) KKP and (c) KKA).

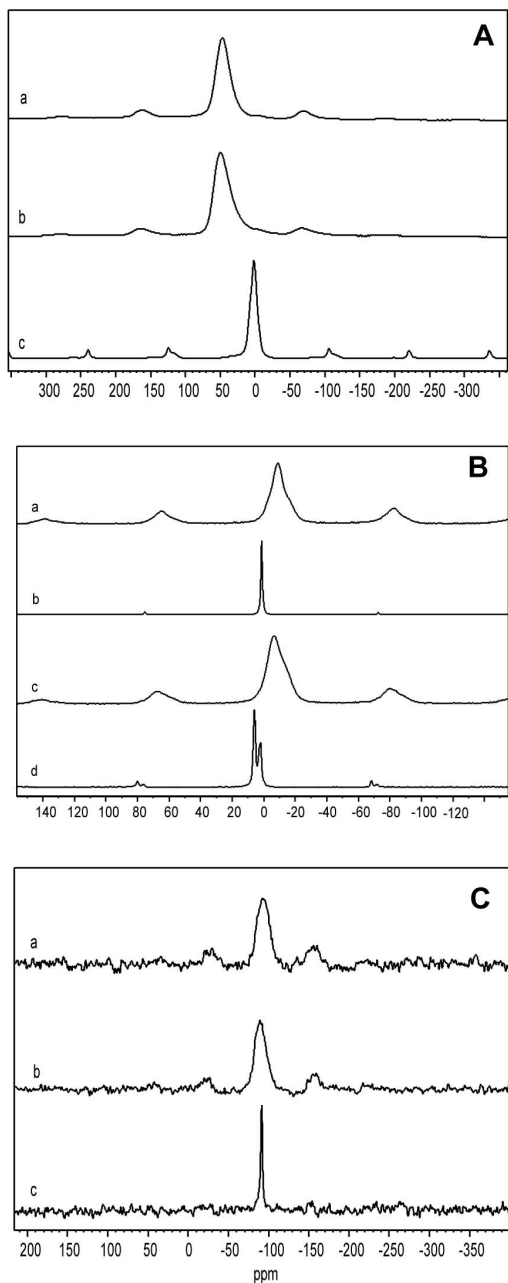


FIG. 6. (A) ^{27}Al NMR spectra of: (a) KAP, (b) KKP and (c) kaolinite; (B) ^{31}P NMR spectra of: (a) KAP, (b) ammonium monohydrogen phosphate, (c) KKP and (d) potassium monohydrogen phosphate; and (C) ^{29}Si NMR spectra of: (a) KAP, (b) KKP and (c) raw kaolinite.

sites of the aluminophosphate (AlPO_4) (Lookman *et al.*, 1977; Zhou *et al.*, 2006; Fernandez *et al.*, 2011; Wang *et al.*, 2013). In the spectrum of KAP (Fig. 6A-a), octahedral sites appeared at $\delta = -3.43$ ppm (9.5% of the Al sites) and a second peak, assigned to the tetrahedral Al of AlPO_4 , was observed at $\delta = 46.54$ ppm (90.5% of the Al sites).

The samples KAP and KKP (Figs. 6B-a,c) showed broad peaks, $\delta -7$ to -10 ppm, in the ^{31}P NMR spectra, corresponding to tetrahedral P, generated by the mechanochemical reaction (Lookman *et al.*, 1977; Zhou *et al.*, 2006).

Each ^{31}P NMR peak in the modified kaolinites was displaced relative to the peaks of the starting salts, ($\text{K}_2\text{PO}_3\text{OH}$, $\delta = 1.27$ ppm, Fig. 6B-d and $(\text{NH}_4)_2\text{PO}_3\text{OH}$ $\delta = 1.88$ and $\delta = 5.87$ ppm, Fig. 6B-c), indicating that new chemical species had formed, probably involving a chemical environment with P bonded to four O–Al groups.

The ^{29}Si MAS-NMR spectra of KAP (Fig. 6C-a) and KKP (Fig. 6C-b) both displayed broad peak doublets, the first between $\delta = -89.00$ and $\delta = -94.00$ ppm, corresponding to Si bonded to four O–Al groups and the second between $\delta = -91.00$ to -96.00 ppm, corresponding to Si bonded to three O–Al groups (Wang *et al.*, 2013). Broad peaks in the MAS-NMR spectra of products relative to starting materials (Fig. 6C-c) are common in synthetic materials containing Si, Al and P. The changes in the chemical environment of the nuclei in these MAS-NMR spectra are very useful in explaining the slow-release behaviour.

The nutrient release curves, with error bars generated from the experiments performed in triplicate, showed two main release steps. The first step is fast and then equilibrium is attained slowly, within ~ 6 h (Fig. 7). For the KAP sample there was also loss of nitrogen ($\sim 50\%$) from the decomposition of ammonium cations into ammonia during milling. The KKP sample displayed slower release behaviour compared with the KAP, probably due to the intrinsic characteristics of each phosphate salt. The release behaviour was much slower for phosphorus, probably because this nutrient interacts more strongly, for example, with aluminium atoms.

The milling of kaolinite with ammonium or potassium monohydrogen phosphate using a high-energy ball mill, with a rotation of 6.708 g (400 rpm) for 3 h, develops amorphous structures that retain reactive species derived from the soluble salts and these species can be released slowly later.

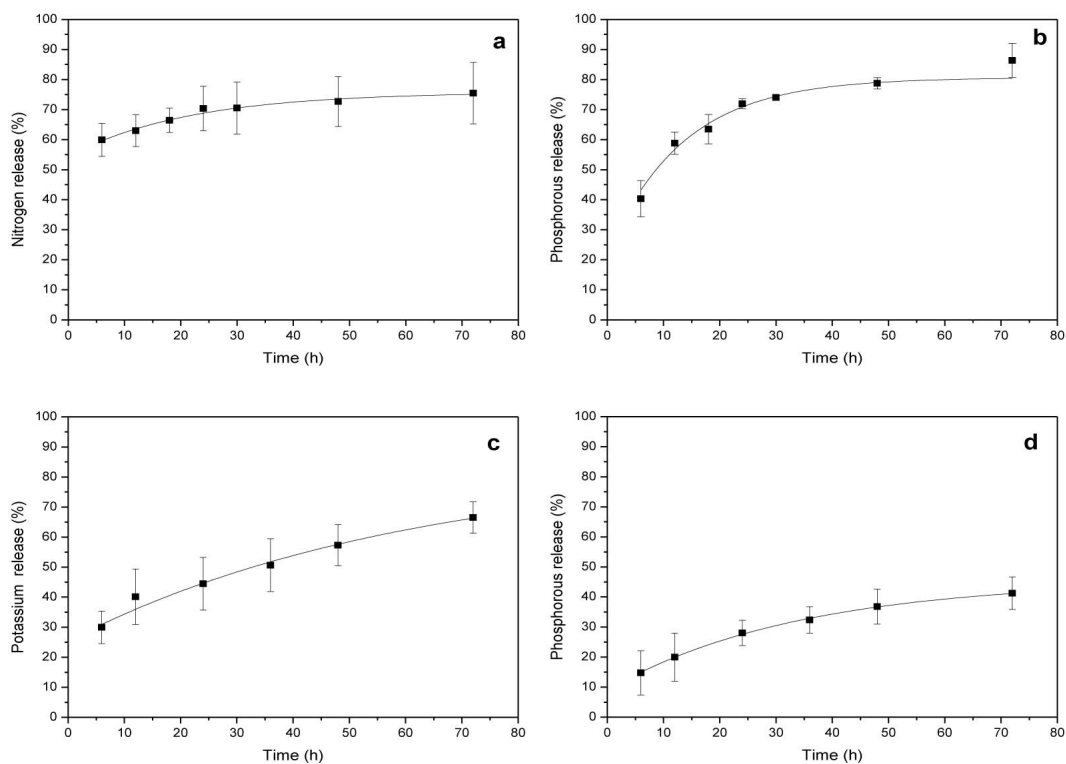


FIG. 7. Release curves of: (a) nitrogen and (b) phosphorus from KAP and (c) potassium and (d) phosphorus from KKP.

This procedure increases the potential of these materials as slow-release fertilizers, especially in the case of flooded crops, according to the release procedure adopted. The rate of release of the nutrients depends on both the milling conditions (time and rotation) and the reagent used. Although the same milling conditions were used in both cases, the phosphorus release results were distinct. This demonstrates that the phosphate salts have different reactivities with the amorphous materials derived from the kaolinite.

It is important to emphasize that the Al and Si constituents of the kaolinite can also be released into solution, which does not occur with the original clay mineral. To overcome the problem of Al release, which can be a potential problem in the soil, studies of the replacement of kaolinite by talc ($Mg_3Si_4O_{10}(OH)_2$), a 2:1 phyllosilicate without layer charge, have been initiated. The X-ray diffraction patterns obtained after preliminary experiments on grinding the talc indicated that the talc structure is also susceptible to amorphization

enabling its potential use as a component in slow-release fertilizers (data not shown).

CONCLUSIONS

Kaolinite ground in a high-energy ball mill with ammonium or potassium monohydrogen phosphate at a 1:1 mass ratio produced amorphous materials. The FTIR spectroscopic and thermal analysis (simultaneous TGA/DTA) results confirmed the mechanochemical dehydroxylation, while SEM observations showed a decrease in particle size and the absence of any characteristic morphology; thus corroborating the XRD, FTIR and TGA/DTA results. The amorphous state cannot explain the release behaviour, but ^{29}Si , ^{31}P and ^{27}Al MAS-NMR measurements showed clearly that new species were being formed by reactions that were combining the elements originally present in the kaolinite and the phosphates.

In the present study drastic leaching conditions were used that were comparable to those in flooded

soils, suggesting that this release process may be very prolonged when applied in soils. For all cases, the procedure is viable for obtaining potential slow-release fertilizers, mainly for phosphorus and potassium as ammonia is evolved. A range of materials can be produced on demand, since the release processes are affected strongly by the milling conditions. The influence of these parameters and the use of alternative raw materials to be milled with soluble phosphates in various proportions will be the subject of future work.

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