

## Solid-State Mechanochemical Synthesis of Kaolinite–Urea Complexes for Application as Slow Release Fertilizer

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### ABSTRACT

This study investigated a mechanochemical (MC) process for synthesizing a slow-release urea fertilizer by co-grinding the starting materials of  $(\text{NH}_2)_2\text{CO}$  and amorphous kaolinite in a planetary ball mill. The tests with kaolinite contents ranging from 25 to 75 wt. %, milling time ranging from 1 (h) to 3 (h) and mill rotational speeds from 200 to 700 rpm were performed to evaluate the incorporation of  $(\text{NH}_2)_2\text{CO}$  and release of nitrogen into the solution. The analyses conducted using XRD, TGA, FT-IR and KNDU (Kjeldahl Nitrogen Determination Unit) indicated that the MC process was successfully applied to incorporate  $(\text{NH}_2)_2\text{CO}$  into the amorphous kaolinite structure. The release of nitrogen from the system (kaolinite- $(\text{NH}_2)_2\text{CO}$ ) when dispersed in water for 24 h reached up to 20% at 25% wt of kaolinite. Moreover, under the milling speed conditions for the system (kaolinite- $(\text{NH}_2)_2\text{CO}$ ), release of nitrogen reached between 25 and 40%. These results indicated that the MC process can be developed to allow amorphous kaolinite to act as a carrier of nitrogen nutrients to be released slowly for use as fertilizer.

**Keywords:** mechanochemical; ball milling; slow-release; kaolinite; urea.

### INTRODUCTION

Elemental nitrogen is considered to be one of the most important components in commercial fertilizers as well as a major nutrient source for food and biomass production in agriculture. However, considering the energy required for its synthesis, nitrogen fertilizers encounter high monetary costs. This is due to the fact that 50–70% of the nitrogen content in conventional fertilizers is lost to the soil through leaching and enhanced by the low nitrogen utilization efficiency (NUE) of plants (Kottegoda *et al.*, 2013). The leaching of nitrogen can occur as water-soluble nitrates, emission as ammonia and nitrogen oxides, and soil microorganism-mediated incorporation into the soil organic material over time. The nitrate in agriculture soils moves into the reduced zone, where it is rapidly converted by the denitrifying bacteria to  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases which are unsuitable for, e.g. rice plants. Denitrification is generally reported as a major reason for the low efficiency

of applied ammonium fertilizers (Kottegoda *et al.*, 2013; Kottegoda *et al.*, 2011).

The loss of nitrates upon using fertilizers by leaching is most noticeable in the soils with high percentage of sand. Recent studies suggest that 15–45% of the surface-applied ammonium-N fertilizers may be lost in the nitrification-denitrification processes. The low NUE is attributed mainly to ammonia volatilization, denitrification, leaching, and run off losses (Jones *et al.* 2013).

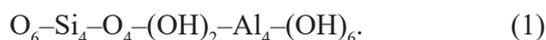
Many attempts to increase the NUE value in conventional fertilizer formulations have been reported (Zhao *et al.*, 2003; Wang *et al.*, 2006; Li *et al.*, 2007). Studies show that the control and slow released fertilizers (CRF/SRF) can improve the efficiency of using fertilizers effectively. Upon using lesser quantities, CRF and SRF can reduce the damage to the environment and ecology making them environmentally friendly fertilizers with minimal pollution. Therefore, CRF and SRF contribute efficiently to the loss of control of

fertilizers (Zhao et al., 2003; Wang et al., 2006; Li et al., 2007).

There are hundreds of different clay minerals with different structures and many contain neutral or charged layers with various elemental composition. Some clay minerals possess very important properties such as those based on layered compounds (LeBaron et al., 1999). One of the most important properties of layered compound is the capacity to intercalate species (neutral atoms, ions or molecules) into the inter-layer spaces. The study of intercalation reactions in clay minerals is a very large research field (Gardolinski, 2000).

One of the famous applications of nanostructured materials such as clays to develop SRF have been studied in recent years. The layers of nanostructured clay minerals have large active surface areas which are exploited to provide enhanced surface interaction with the fertilizer elements. Mechanochemical activation of layered minerals, especially clay minerals, has been studied extensively 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 (Zhang et al., 2012; Hrachova et al., 2007; Vizcayno et al., 2010; Sun, 2011; Mako et al., 2014; Borges et al., 2015).

kaolinite is a type of a clay mineral consisting mainly of hydrated aluminum silicate or kaolinite formed through hydrothermal alteration of feldspar and muscovite, usually containing quartz (Solihin et al., 2011). kaolinite is usually represented by the  $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$  formula and/or other forms, including  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_7\text{Si}_2 \cdot 2\text{H}_2\text{O}$ , which builds up by a sheet structure composed of  $\text{SiO}_4$  tetrahedral sheets, and  $\text{Al}(\text{O},\text{OH})_6$  octahedral sheets ( $[\text{Si}_2\text{O}_5]^{2-}$  sheet and  $[\text{Al}_2(\text{OH})_4]^{2+}$  sheet) with pseudo-hexagonal symmetry that are created from planes, which are occupied as follows:



Kaolinite is an important industrial mineral, which is used in many applications, including paper filling and coating, refractory, ceramic, food additives and was used as the reservoir and cache of nutrient elements (Solihin et al., 2011).

Urea is a fertilizer material which can be used for direct application to crops or in the preparation of blended fertilizers (Roshanravan et al., 2014). Man *et al.* (2004) intercalated urea into

the montmorillonite layers to prepare a controlled-release urea-based fertilizer. According to the documented result, about 80% of the intercalated urea was decomposed in water within 30 days (Man et al., 2004). Additionally, Urena-Amate et al. (2011) investigated a formulation of nitrate modified hydrotalcite-like layered double hydroxide (LDH) and hydroxypropyl methylcellulose (HPMC) as a nitrogen based controlled release fertilizer. The system with the highest LDH/HPMC ratio produced the slowest release ratio (around 87%) after 180 hours in the simulated soil solution (Man et al., 2004). The intercalation of kaolinite by urea has been studied in numerous works (Valaskova et al., 2007; Rutkai et al., 2009). However, previous studies have focused only on the intercalation of urea as the guest molecule between the clay nano-layers rather than on the nitrogen release behavior, which is the main focus of this section.

In the current study, we aimed at producing potential slow-release fertilizers with nitrogen, phosphorus and urea ( $(\text{NH}_2)_2\text{CO}$ ). A milling operation was performed for the kaolinite – Urea system to completely reduce the kaolinite structure to amorphous phase. A mechanochemical reaction was used to obtain the necessary chemical bonding between  $\text{NH}_2-\text{Al}-\text{Si}-\text{P}-\text{O}$  as amorphous phase. The new product was targeted to give a water-insoluble property so the release of nitrogen from urea nutrients into the soil can be controlled and offered as SRF or CRF fertilizer. Different milling conditions and kaolinite addition ratios were investigated to obtain the optimum milled products with desired properties.

## METHODOLOGY

### Materials and mechanochemical process

The mechanochemical reactions between high-purity kaolinite from Wadi Araba-Jordan,  $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$  (Bayook et al., 1992; Barjous et al., 1997) and urea ( $\text{CON}_2\text{H}_4$ ) as commercial fertilizer were investigated. A 6.0 g sample mixture of starting materials with varying weight ratios (see Table 1) and ball/sample weight ratio of about 10 was milled for 120 min at fixed milling in a planetary ball mill (Pulverisette-7, Fritsch, Germany), which had two mill pots (45 cm<sup>3</sup> inner volume each) made of zirconium with 6 Zirconia-balls of 15 mm diameter. In order to avoid excessive heat

during milling at all experiments, the operation was conducted by alternating 10 min of milling with 5 min of rest.

Three series of experiments were performed to observe the effect of different mole ratios of kaolinite: urea, milling speed and duration on the nutrient released of samples. Table 1 shows three different chemical compositions (mole ratios) that were investigated.

The milling speed used in this experiment ranged between 200 and 700 rpm at 3:1 mole ratio of kaolinite: Urea and milling time was fixed at 120 min. The milling time for the complex was ranged between 60 and 180 min when (3-kaolinite:1-urea) mole ratio 600 rpm milling speed were used.

### Characterization

Before and after milling, the samples were examined with X-ray diffraction (XRD, Rigaku, Japan), using Cu K- $\alpha$  radiation within a recorded range of  $2\theta$  from  $5^\circ$  to  $90^\circ$ . A Fourier transformation infrared spectrometer (FTIR, NEXUS, EPS-870) was used to analyze the prepared samples using an advanced sensor (not KBr method) scanned from  $4000$  to  $400\text{ cm}^{-1}$  with a resolution of  $2\text{ cm}^{-1}$ . A thermal gravimetric/differential thermal analysis (using STA-409 PC, NETZSCH) was carried out in an  $\text{N}_2$  atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $1000^\circ\text{C}$ .

Leaching experiments on the ground samples in distilled water were carried out in a 100-mL glass beaker with the parameters at room temperature: 1 g of ground sample; 20 mL of distilled water and leaching times was 24 h, 168 h and 336 h for urea. After leaching, the solid-liquid separation was performed by vacuum filtration with a filter paper of  $0.45\text{ }\mu\text{m}$  pore size. The quantity of nutrient released in the filtrate was measured using Kjeldahl Nitrogen Determination to determine the total nitrogen released from urea.

## RESULTS AND DISCUSSION

It was possible to study the influence of speed and time of milling in the high-energy ball-mill. For this reason, a series of experiments were performed, which involved the milling of kaolinite and urea to establish processing conditions that maximize the slow-release behavior of nutrient.

The XRD patterns of kaolinite- $(\text{NH}_2)_2\text{CO}$  (3:1 weight ratio) sample mixture milled for 120 min at 600 rpm mill speed (Fig. 1) indicated that the starting materials were completely reduced to amorphous state. Characteristic peaks of urea shifted in products, indicating that higher mill speeds and sufficient amount of the kaolinite content were required to reduce the starting materials to amorphous state and allow incorporation of  $(\text{NH}_2)_2\text{CO}$  into the kaolinite structure.

### Effect of starting materials mass percentage for mechanochemical synthesis of kaolinite-urea system

The FT-IR spectra presented in Figure 2 showed that at different mass ratio of kaolinite to  $(\text{NH}_2)_2\text{CO}$ , characteristic spectrums corresponding to  $(\text{NH}_2)_2\text{CO}$  had disappeared in the milled products like as kaolinite peaks ranged from  $3620$ – $3686\text{ cm}^{-1}$  that exist in Fig. 2a, which could suggest that  $(\text{NH}_2)_2\text{CO}$  has been incorporated into amorphous structure of kaolinite.

The samples (25% kaolinite, 50% kaolinite and 75% kaolinite) showed that the mechanochemical amorphization was related to the dehydroxylation of the kaolinite, as the typical bands of the inner surface hydroxyls ( $3700$ – $3622\text{ cm}^{-1}$ ) and internal octahedral layer hydroxyls ( $3620\text{ cm}^{-1}$ ) had disappeared. According to the generally accepted concept of mechanochemical-dehydroxylation, these hydroxyl groups form coordinated water molecules by proton transfer. Clear band on  $(\text{NH}_2)_2\text{CO}$  spectrum at ( $1146\text{ cm}^{-1}$ ) had been up field shifted in 25% kaolinite and 50% kaolinite samples and to be disappeared in (75% kaolinite) sample which indicated to completely intercalation of  $(\text{NH}_2)_2\text{CO}$  in kaolinite. Furthermore, in the region around  $1000\text{ cm}^{-1}$ , 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 mass loss characteristics behavior of the kaolinite mixtures  $-(\text{NH}_2)_2\text{CO}$  (different weight percentages) milled for 120 min at fixed mill speeds (600 rpm) is shown in Figure 3. One mass loss peak down at  $180^\circ\text{C}$  seen clearly only for

**Table 1.** Chemical composition of starting mixture investigated

Mole ratio			
Kaolinite : Urea	(1:3)	(1:1)	(3:1)

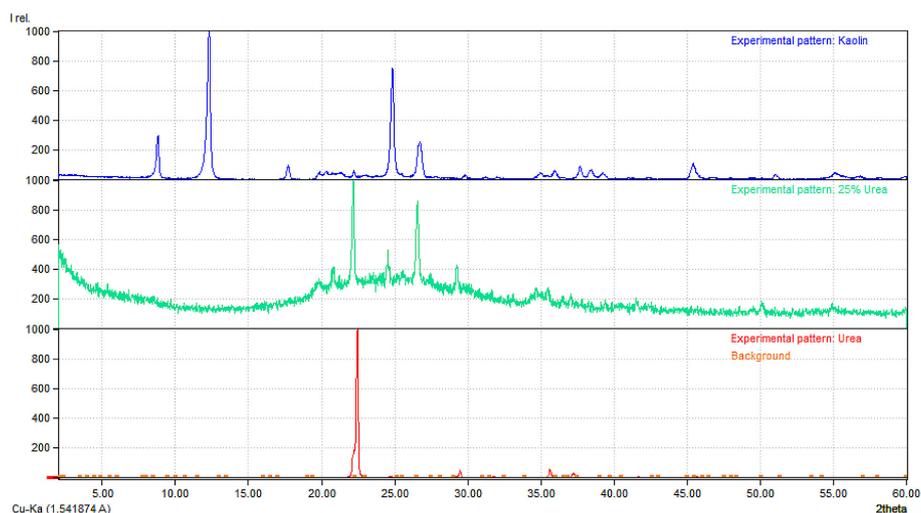


Fig. 1. XRD patterns of kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 wt ratio) sample mixtures milled for 120 min at 600 rpm

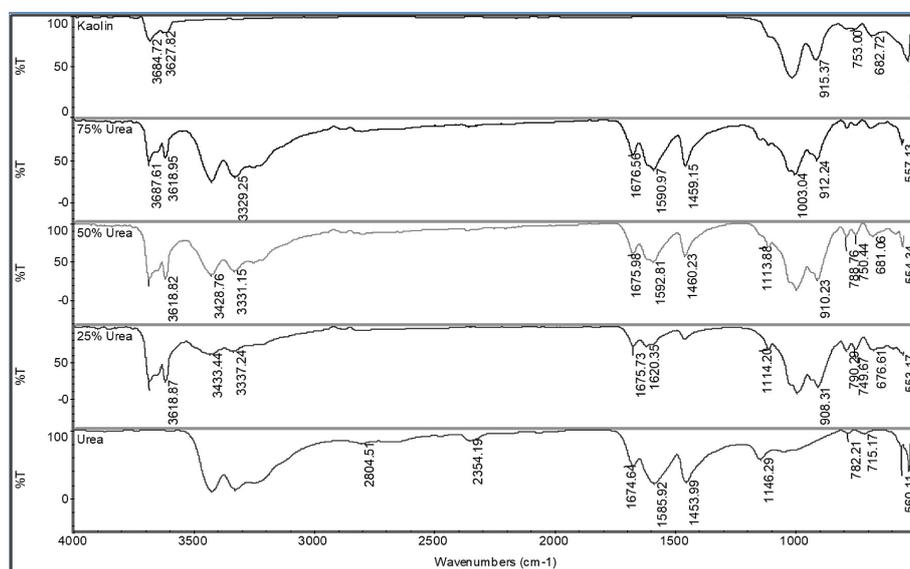


Fig. 2. FTIR spectra of samples (kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO) (a) without milling for different mole ratios, and (b) milled at speed 600 rpm for different mole ratios

sample mixture (25% kaolinite: 75% (NH<sub>2</sub>)<sub>2</sub>CO) with complete incorporation of (NH<sub>2</sub>)<sub>2</sub>CO into the amorphous structure of the kaolinite system. On the other hand, two mass loss had appeared when the (50%:50%) and (75% kaolinite:25% (NH<sub>2</sub>)<sub>2</sub>CO) mole ratios were used. Its appearance during the thermal decomposition indicates the mechanochemical reaction did not finish and there was some urea that did not intercalate with kaolinite; it also illustrates that the milling process at high mass ratio for kaolinite: (NH<sub>2</sub>)<sub>2</sub>CO can promote the synthesis of a N-Si-P-O system.

The nutrient release behavior when dispersed in water for the sample mixtures milled with varying content of kaolinite is shown in Figure 4. At 25 wt. % kaolinite addition, the release of nutrients

dispersed in water reached over 81% and closer to 100% but decreased to between 30 and 50% for the kaolinite content at 50 wt. % and was further reduced to below 22% for sample mixture with kaolinite content at 75 wt. %. The decrease of nutrients release into solution indicated that (NH<sub>2</sub>)<sub>2</sub>CO on impact of milling was incorporated into Al-Si-O network.

#### Effect of milling speed on mechanochemical synthesis of kaolinite - (NH<sub>2</sub>)<sub>2</sub>CO system as SRF

The effect of mill rotational speed on amorphization of the kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 wt ratio) sample mixture is shown in Figure 5. The milling time for all experimental runs was fixed

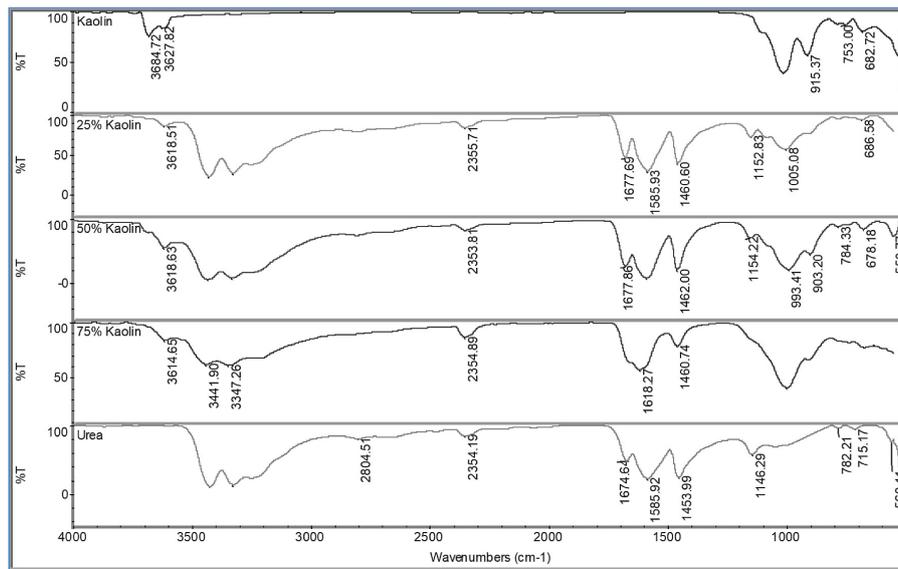


Fig. 3. TGA patterns of (kaolinite –  $(\text{NH}_2)_2\text{CO}$ ) (different weight ratio) sample mixture milled for 120 min at fixed mill rotational speeds (600 rpm)

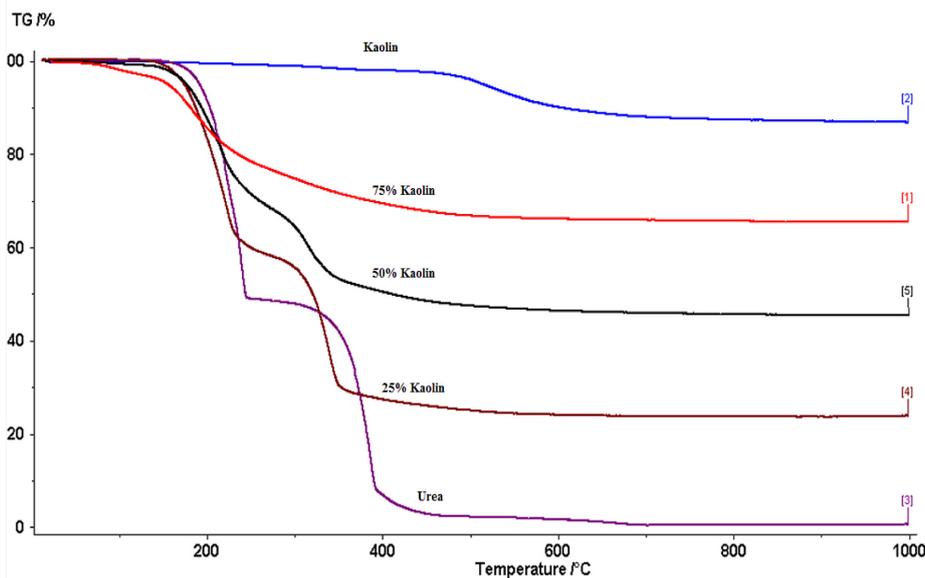


Fig. 4. Nutrients release profile of kaolinite- $(\text{NH}_2)_2\text{CO}$  sample system with varying amounts of kaolinite (wt %) milled for 120 min at 600 rpm

at 120 min and the mill rotational speeds ranged between 200 and 700 rpm. The FT-IR spectra showed that at lower mill rotational speeds, ranging from 200 to 400 rpm, the characteristic spectrums corresponding to  $(\text{NH}_2)_2\text{CO}$  remained in the milled products like as kaolinite peaks ranged from 3620–3686  $\text{cm}^{-1}$ . However, disappearance of previous peaks at mill speeds above 400 rpm indicated that the starting samples were reduced to amorphous state, which could suggest that  $(\text{NH}_2)_2\text{CO}$  had been incorporated into amorphous structure of Kaolinite.

Moreover, the N-H broad bands located between 3470–3200  $\text{cm}^{-1}$  were gradually decreased, after the gradual increase of samples milling, which illustrated the formation new product, i.e. a kaolinite- $(\text{NH}_2)_2\text{CO}$  system when high milling speed used.

Additionally, the thermal gravimetric analysis presented in Figure 6 proved that the measured mass loss of 11.5%, due to the thermal dehydroxylation of the Kaolinite, is in good agreement with the expected value of 13.96%, thus proving the good purity of the starting Kaolinite [14].

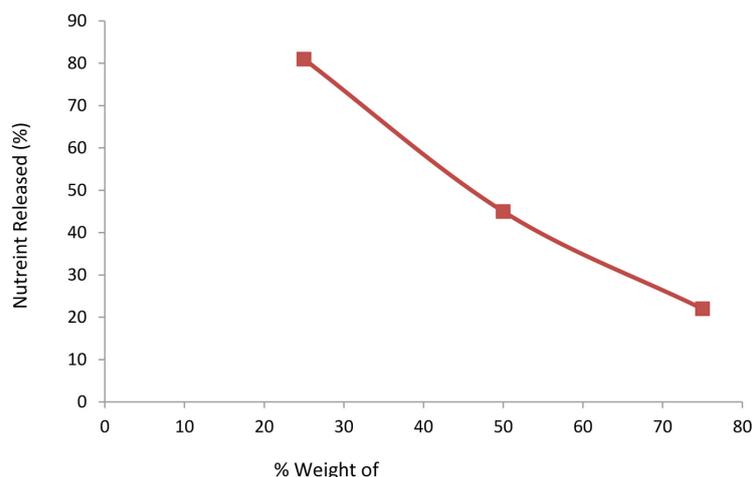


Fig. 5. FTIR spectra of samples (kaolinite- $(\text{NH}_2)_2\text{CO}$ , (3:1) mole ratios milled at different rotating speed for 2 (h)

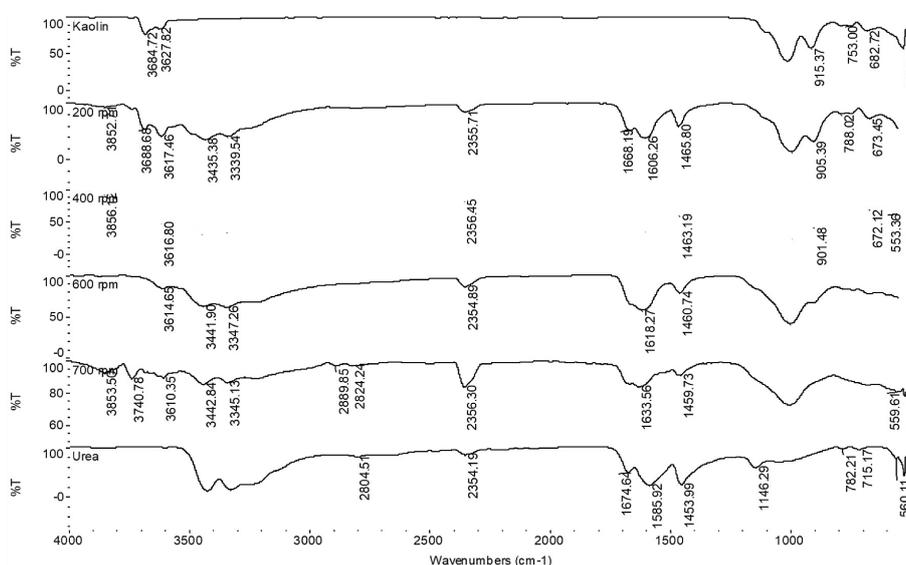


Fig. 6. TGA patterns of kaolinite- $(\text{NH}_2)_2\text{CO}$  (75%:25% weight ratio) sample mixture milled for 2 (h) at different mill rotational speeds

Basically, the urea molecules decompose in two steps, with endothermic peaks at 225°C, 300°C and 425°C for (kaolinite–urea) milled at 200 rpm. However, decomposing into one step for sample milled at 700 rpm at 150°C (Fig. 6), which illustrates that the intercalation reaction is facilitated at high milling speed. The mass-loss characteristics of the starting materials were not observed in the (kaolinite-urea) samples milled at over 400 rpm, which attests to their destruction during grinding; the observed behavior was in agreement with other instrumental techniques, which showed the formation of amorphous phases derived from the mixture of the reagents.

The nutrients release behavior of kaolinite- $(\text{NH}_2)_2\text{CO}$  (3:1 wt ratio) samples as a function of mill rotational speeds when dispersed in water

for 24 h is shown in Figure 7. For the samples milled at 200 rpm, urea was close to complete dissolution into water. This result corresponds well with FT-IR data (Fig. 5), where the easily soluble  $(\text{NH}_2)_2\text{CO}$  patterns continued to remain in the milled products and this indicated that the nutrients have not yet been incorporated into the kaolinite structure. For the sample mixtures milled at 400 rpm and above, where complete amorphization was observed, the subsequent release of nutrients decreased and reached an average of around 20–30% in 24 h. This result showed that higher mill rotational speeds were required to reduce the starting materials to amorphous phase and allow incorporation of the nutrients into the kaolinite structure.

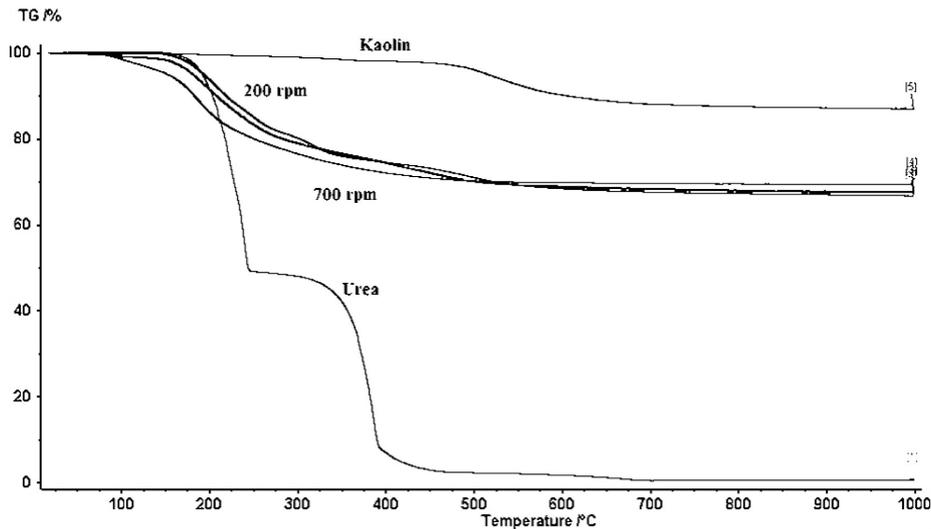


Fig. 7. Nutrients release profile of kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO(3:1 wt ratio) sample mixtures milled for 120 min at different mill speeds and dispersed in water for 24 h

### Effect of milling time on mechanochemical synthesis of (kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO) as SRF

The FTIR spectra of (kaolinite:(NH<sub>2</sub>)<sub>2</sub>CO) samples have a ratio 3:1 that milled at t 600 rpm for several different durations are depicted in Figure 8. It can be seen that when the time of rotational milling increased, the bond vibration intensity decreased until disappearance, like in the peak of around 915 cm<sup>-1</sup> in kaolinite and broad peak of N-H bonds in urea at 3200–3400 cm<sup>-1</sup>. Additionally, the peaks with high absorption intensity, at (3620–3690 cm<sup>-1</sup>), could not be observed on the different milled samples, indicating that the intercalation take place. When the duration reached 120 min and then 180 min, the intensity of the peaks decreased. However, disappearance of peaks at milling time above than

120 min indicated that the starting samples were reduced to amorphous state, which could suggest that (NH<sub>2</sub>)<sub>2</sub>CO has been incorporated into amorphous structure of kaolinite.

The mass-loss characteristics of the starting materials were not observed in the milled samples of urea Figure 9, which attests to their destruction during grinding; the observed behavior agreed with other instrumental techniques, which showed the formation of amorphous phases derived from the mixture of the reagents.

The release profile of (NH<sub>2</sub>)<sub>2</sub>CO nutrients for the kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 wt ratio) sample mixtures milled at different mill time and dispersed in water for 24 h is shown in Figure 10. For the sample mixtures prepared at 180 min, the release of urea reached over 20–30% indicating that higher mill duration is required to effect

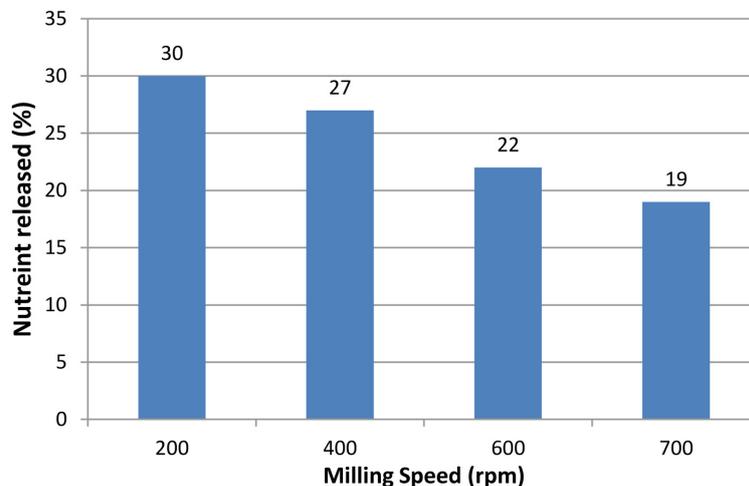


Fig. 8. FTIR spectra of samples (kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO, (3:1) mole ratios) milled at speed 600 rpm for different duration

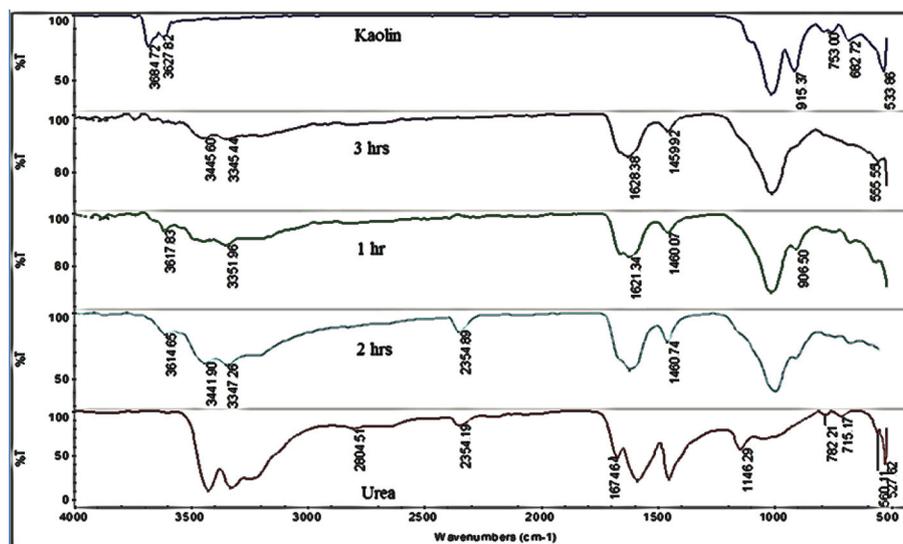


Fig. 9. TGA patterns of Kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 wt ratio) sample mixture milled at speed 600 rpm for different milling time

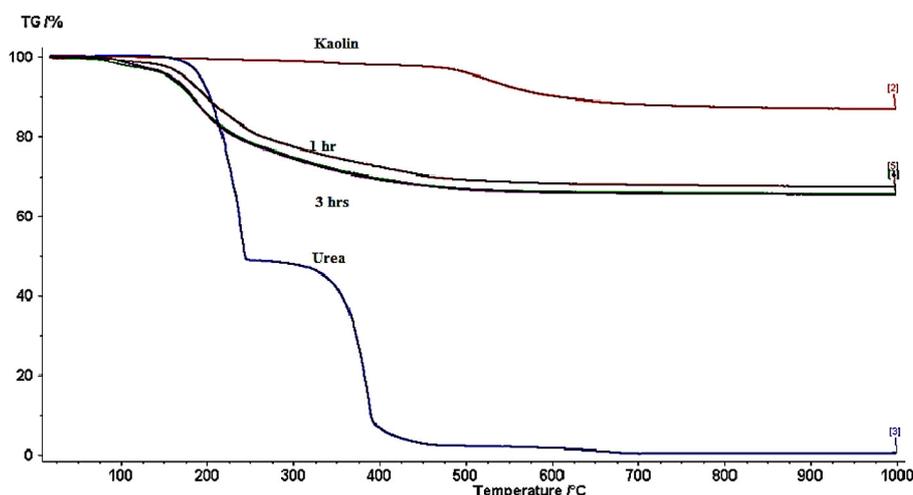
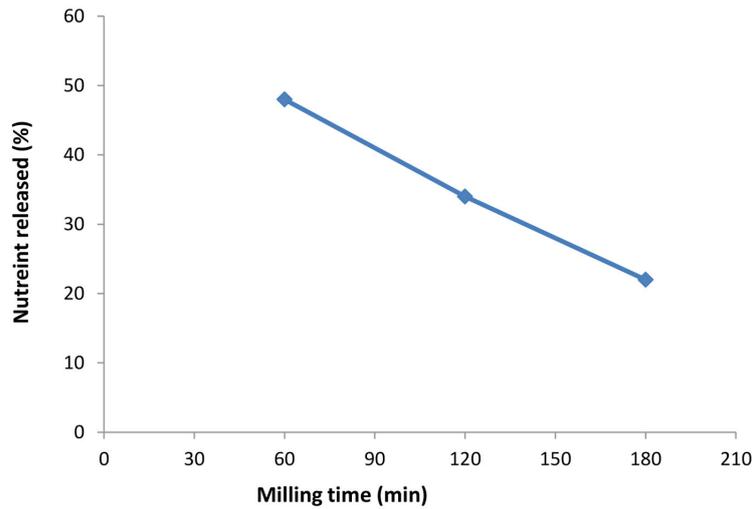


Fig. 10. Nutrients release profile of kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO(3:1 wt ratio) sample mixtures milled at 600 rpm for different milling time and dispersed in water for 24h

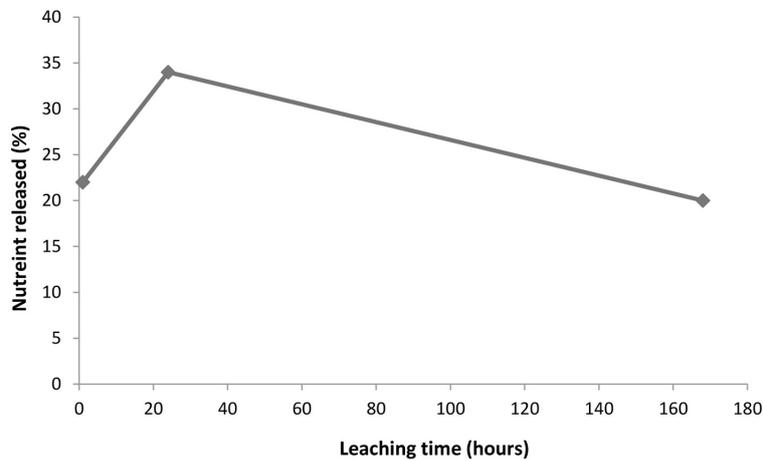
complete amorphization of starting materials to allow incorporation of (NH<sub>2</sub>)<sub>2</sub>CO into the amorphous kaolinite structure. When the milling time was decreased from 180 to 120 rpm, the release of (NH<sub>2</sub>)<sub>2</sub>CO nutrients into solution significantly increased, reaching around 30–40% at 600 rpm and remained around 45% for the samples obtained from milling at 600 rpm for 60 min indicating that some (NH<sub>2</sub>)<sub>2</sub>CO was incorporated into amorphous structure of kaolinite.

The release profiles of (NH<sub>2</sub>)<sub>2</sub>CO nutrients for the kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 weight ratio) sample mixtures milled at 700 rpm for fixed milling time 120 min and dispersed in water for different duration are shown in Figure 11.

Figure 12 shows the kaolinite-(NH<sub>2</sub>)<sub>2</sub>CO (3:1 weight ratio) sample mixtures dispersed in distilled water. For the sample mixtures leached only for 60 min, the release of urea reached over 20–25% indicating that sufficient duration is required to achieve complete amorphization of starting materials to allow incorporation of (NH<sub>2</sub>)<sub>2</sub>CO into the amorphous kaolinite structure. When dispersing time was increased from 1 to 24 h, the release of (NH<sub>2</sub>)<sub>2</sub>CO nutrients into solution significantly increased, reaching around 30–40% at and other decreased for about 20% for the samples obtained by leaching for 168 h, indicating that (NH<sub>2</sub>)<sub>2</sub>CO was incorporated into the amorphous structure of kaolinite.



**Fig. 11.** Nutrients release profile of kaolinite-  $(\text{NH}_2)_2\text{CO}$  (3:1 wt ratio) sample mixtures milled At 600 rpm for 120 (min) milling time and dispersed in water for varied time 1, 24 and 168 h



**Fig. 12.** Kaolinite- $(\text{NH}_2)_2\text{CO}$  (3:1 weight ratio) sample mixtures dispersed in distilled water

## CONCLUSIONS

The release behavior experiments for non-coated intercalated urea-kaolinite samples revealed a dramatic decrease in the urea release after intercalation of urea into kaolinite. The incorporation of  $(\text{NH}_2)_2\text{CO}$  compound into the structure of kaolinite was successfully achieved through mechanochemical route by a milling operation. The amount of kaolinite and its degree of amorphization played an important role in the incorporation process.

The findings in the present study can be summarized as follows:

a) A mill rotational speed of at least 400 rpm was required to reduce all starting materials to amorphous state. Sufficient ball movement and collision was necessary for milling of the samples charged in the mill pots.

b) Slow release behavior of the nutrients incorporated into kaolinite structure when dispersed in water was observed for sample mixtures milled at 400 rpm and greater.

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