An FTIR Spectroscopic Study of a Novel Kaolinite-NPK Mixture

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Abstract: In the present study, Fourier Transform Infrared (FTIR) spectroscopic characterization of a novel mixture of kaolinite-NPK is described. Kaolinite is an environmentally friendly substance that exhibits good structural properties when used as a carrier of chemical fertilizers. Mixtures of kaolinite and NPK fertilizer were prepared by mechanochemical ball milling with three different mass ratios (Kaolinite : NPK = 1:3, 1:1 and 3:1). The milling parameters were varied in order to obtain the best mixture consistency. These include milling time (60, 120, and 180 min) and rotational speed (200, 400 and 700 rpm). The studied NPK fertilizers are urea (CON_2H_4), ammonium phosphate ($(NH_4)_2HPO_4$), and potassium dihydrogen phosphate (KH_2PO_4). The result indicated that a mass ratio of kaolinite: NPK of 3:1 and a milling duration of 120 min at a rotational speed of 600 rpm represent the most suitable conditions to synthesize a novel kaolinite-NPK mixture. A possible application of this mixture is the use as a slow-release fertilizer.

Keywords: NPK fertilizers, Kaolinite, Mechanochemical, Milling, FTIR.

دراسة التوصيف الطيفي بتقنية فورير لتحويل الأشعة تحت الحمراء لمزيج جديد من الكاولين والسماد الكيميائي المكون من النيتروجين والفسفور والبوتاسيوم

الملخص: تم في هذه الدراسة دراسة التوصيف الطيفي بتقنية فورير لتحويل الأشعة تحت الحمراء (ف.ت.أ.ت.ح) لمزيج جديد من الكاولين والسماد الكيميائي المكون من النيتروجين والفسفور والبوتاسيوم (ن.ف.ب). تعتبر مادة الكاولين مادة صديقة للبيئة وكذلك فإنها تُظهر خصائص هيكلية جيدة عند استخدامها كحامل للأسمدة الكيماوية. في هذا البحث، تم تحضير خلطات من الكاولين والأسمدة النيتروجينية بواسطة الطحن الميكانوكيميائي بالكرات لثلاثة نسب ذات كتلة مختلفة (نسبة الكاولين إلى سماد (ن.ف.ب) = 1:3 و1:1 و3:1). وقد استخدمت عوامل طحن مختلفة للحصول على أفضل تناسق للخليط واشتملت على ما يلي: وقت الطحن (60 و120 و180 دقيقة) وسرعة الدوران (200 و400 و700 دورة في الدقيقة). كانت أسمدة (ن.ف.ب) المستخدمة في الدراسة هي اليوريا (CON2H4) وفوسفات الأمونيوم (NH4)2HPO4) وفوسفات البوتاسيوم ثنائي الهيدروجين (KH2PO4). أوضحت نتائج الدراسة أن نسبة الكتلة 3:1 من الكاولين إلى سماد (ن.ف.ب) خلال مدة الطحن 120 دقيقة بسرعة دوران 600 دورة في الدقيقة تمثل الظروف الأكثر ملاءمة لتجميع خليط جديد من الكاولين والسماد والذي يمكن استخدامه كسماد بطيء التحلل في التربة.

1. Introduction

With the population growth and rapid urbanization, controlled and efficient fertilization is essential in modern agriculture in order to improve crop yields. However, conventional and commonly used chemical fertilizers tend to dissolve in the soil at a much faster rate than plants intake. The resulting imbalanced fertilization leads to a rapid release of nutrients from the soil into groundwater. In addition to the loss of valuable fertilizers, the leak is found to cause many environmental concerns [1]. For a sustainable agriculture, slow-release fertilizers (SRF) in which nutrients are slowly released and hence synchronized with the growth rate and physiological need of plants is one of the alternative solutions to fertilization issues.

NPK fertilizers comprise primarily of the three primary nutrients required for healthy plant growth (Nitrogen, Phosphorus and Potassium). The Jordanian agriculture industry relies heavily on the use of DAP (di ammonium phosphate) and other NPK fertilizers to meet the demanding food supply and ensure healthy crops.

Most studies on SRF have pointed out that the required amount of nutrients is significantly reduced compared to conventional fertilizers [2-9]. Some researchers recommended the use of SRF in order to reduce N_2O emissions from the agricultural fields in an attempt to reduce its role in climate change [10-11].

Several types of SRF have been prepared based on a wide range of physical and chemical methods including dispersion of fertilizer in a matrix. Among them, Noh et al. described a mineral-based SRF that exhibits charge and crystal structure frameworks protecting nutrients from rapid degradation and hence contributing to the long-term fertility in the soil [12]. To this type of fertilizer, various inorganic clays including kaolinite are used as a nutrient-carrier through a mechanochemical processes, like milling, to produce highly reactive amorphous materials that are capable of reacting with soluble fertilizers such as urea [13-17].

A mechanochemical process is a simple, environment friendly, low-cost milling and mixing technology that does not require chemical solvents. The effectiveness of the mechanochemical synthesis is highly dependent on the mass ratio of carrier to fertilizer and on the milling parameters such as milling speed and milling duration. However, these practical variables have not been extensively tested with SRFs and, to our knowledge, no previous work has been carried out on kaolinite-NPK mixtures as an SRF. In this study, we use the abundantly available and low-cost Jordanian kaolinite as a carrier for our SRF.

In the present study, we use Fourier transform infrared (FTIR) spectroscopy as a reliable technique to study the degree of bonding of NPK chemical fertilizers (NPK) within a mixture of kaolinite-NPK. Since all bonds within molecules vibrate at temperatures above absolute zero as bending and/or stretching, FTIR spectroscopy is a precise overview of the presence of different molecular functional groups and hence molecules. Therefore, different peaks account for different molecules. This is proven by FTIR in the case of dehydroxylation of kaolinite (loss of OH groups).

The mass ratios and milling parameters were varied and tested by FTIR in order to establish the optimal conditions for the mechanochemical synthesis of a novel kaolinite-NPK fertilizer mixture.

The studied chemical fertilizers are urea (CON_2H_4), ammonium phosphate ($(NH_4)_2HPO_4$), and potassium dihydrogen phosphate (KH_2PO_4). The results showed very similar results proving the validity of our technique to synthesize a novel formulation of a slow-release fertilizer (SRF).

2. Experimental

Kaolinite ($Al_2(Si_2O_5)(OH)_4$), as a hydrated aluminum silicate, was obtained from Wadi Araba in Jordan [18-19]. The NPK fertilizers used in this study were of chemical grade reagents: urea (CON_2H_4), diammonium phosphate ($(NH_4)_2HPO_4$), potassium sulfate (K_2SO_4) from Merck and potassium phosphate (KH_2PO_4) from Panreac PRS.

The samples were prepared by co-grinding the kaolinite and one of the different fertilizers at dry conditions using a planetary ball mill (Pulverisette-7, Fritsch, Germany), which had two mill pots (45 cm^3 inner volume each) made of zirconia (ZrO_2) with 7 zirconium-balls of 15 mm diameter. Five grams of the starting materials was put into the vial with the balls, and milled under ambient atmosphere.

Three sets of experiments were designed and performed to observe the effect of different mixing ratios of kaolinite to fertilizer, milling speed and duration on the infrared spectra of synthesized mixtures (Table 1).

To avoid any chemical complications resulting from the excessive heating during the milling processes, the operation was programmed to include a 5-minute rest time for every 10 minutes of continuous milling.

Table 1. Mixture ratios and milling parameters used in the different experiments.

Set	(kaolinite: NPK) mass ratio	Milling speed (rpm)	Milling time (min)
Exp. 1	1:3, 1:1, 3:1	600	120
Exp. 2	3:1	200, 400, 700	120
Exp. 3	3:1	600	60, 120, 180

Infrared spectra of all synthesized samples were recorded using a Fourier transform infrared spectrometer (FTIR, Thermo Nicolet Nexus 870). The samples were diluted in powdered solid KBr (Spectroscopic grade, Sigma-Aldrich). KBr background spectrum was obtained before running each sample. IR spectra were collected in the mid-IR region (500-4000 cm^{-1}) with a spectral resolution of 4 cm^{-1}.

3. Results and Discussion

The IR spectra of kaolinite, NPK and their mixtures are discussed in the first part. The second part presents the results for the effect of varying mass ratios of kaolinite to NPK. The third and fourth parts deal with results of the milling parameters: milling speed and milling duration, respectively.

3.1 IR Characteristics of Kaolinite, NPK And Their Mixtures:

Figure 1 displays the infrared spectra of kaolinite-NPK mixtures. Two types of the hydroxyl functional group can be assigned for kaolinite. The stretching of the inner surface hydroxyl groups occurs at 3688 and 3655 cm^{-1}, whereas the band at 3619 cm^{-1} belongs to the inner hydroxyl group that lie within lamellae in plane common to both tetrahedral and octahedral sheets. The intensity and location of the inner surface hydroxyl groups usually change upon intercalation, whereas the band at 3619 cm^{-1} remains unaffected by intercalation [20-21].

In an ordered kaolinite, four distinct IR bands can be assigned, whereas poorly ordered kaolinite, displays only three bands [22], as can be seen in this study. The Si-O stretching region comprises of stretching bands at 1113, 1000-1003 and 1025 cm^{-1}, and the Si-O bending vibrations at 790, 751 and 688 cm^{-1}. The Al-OH bending vibration at 912 cm^{-1} assigned to the inner hydroxyls.

The most intense bands of urea (CON_2H_4) are the N-H stretchings at 3427, 3339 and 3254 cm^{-1}, the N-H bending vibration at 1591 cm^{-1} and the C-N stretching at 1459 cm^{-1} (Figure 1 A). The band at 1677 cm^{-1} is assigned as the amide vibration, while the band at 1147 cm^{-1} is attributed to NH_2 vibration [23-24].

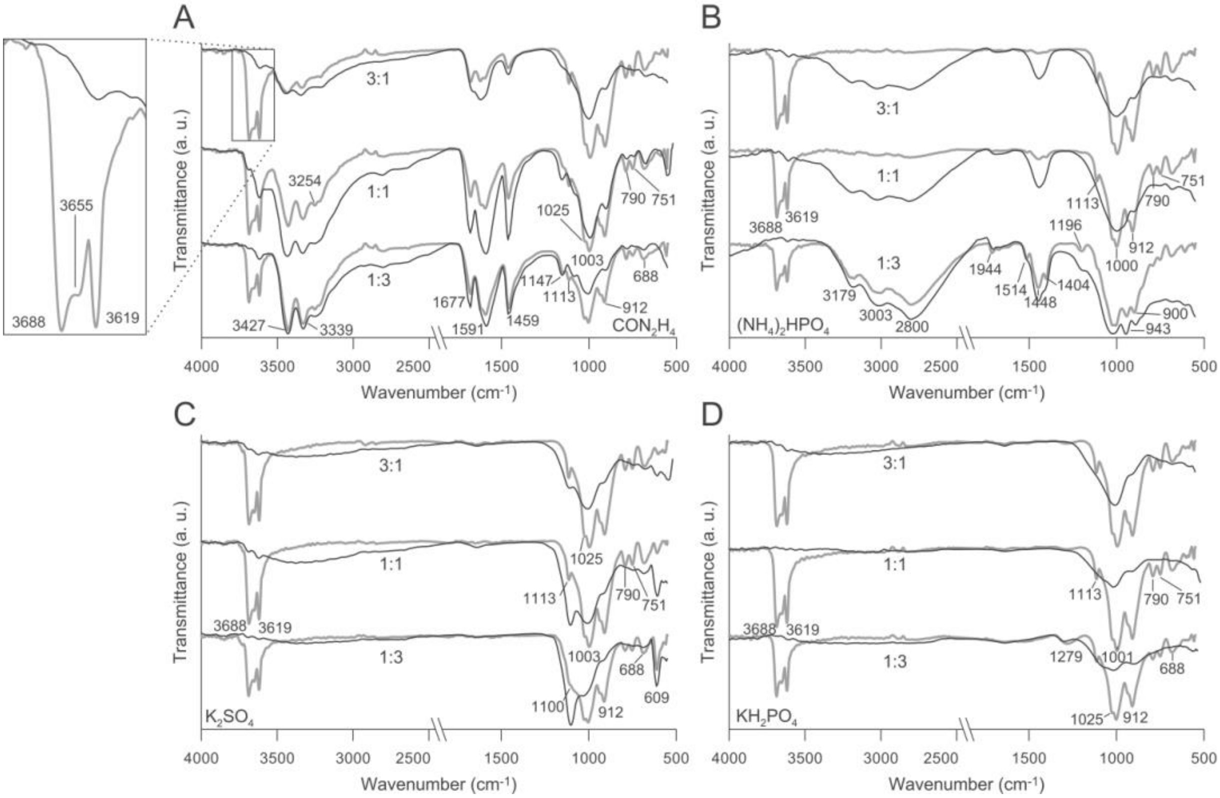

Figure 1. Infrared spectra of original kaolinite-NPK mixtures (light-faced) and the milled samples (bold-faced) are shown. A: urea, B: DAP, C: K_2SO_4, D: KH_2PO_4. The characteristic peaks and the ratios of the kaolinite-NPK (1:3, 1:1, 3:1) are also displayed.

From the IR spectra of DAP ($(NH_4)_2HPO_4$), the presence of vibration due to NH_4 groups is noticed. Two strong bands are observed at 3179 and 3003 cm^{-1} and a mid-band upto 1448 cm^{-1} (Figure 1 B). The band at 2800 cm^{-1} corresponds to the O-H stretching vibration. The O-H bending vibration can be seen at 1196 cm^{-1}. The peak of the PO_4^{3-} group is found at 943 cm^{-1} [25].

The bands of K_2SO_4 appearing at ~1100 and 609 cm^{-1} are assigned to stretching and bending of the sulfate (SO_4) groups [26] as seen in (Figure 1 C).

Figure 1 D shows the spectral profile of KH_2PO_4 with three smooth band peaks at 1279 cm^{-1}, at 1077 cm^{-1} (PO4 vibrations) and at 877 cm^{-1} (($PO_2(H_2)$ vibration) with increasing transmittance values from the highest to the smallest wavenumber regions [27].

3.2 The Effect of Kaolinite-NPK Fertilizer Mass Ratio:

For this part of the experiment, the milling speed and duration were kept constant. Three different mass ratios were studied (kaolinite : NPK = 1:3, 1:1 and 3:1). IR spectra were collected for the mixtures. The spectra show that characteristic peaks of the individual studied fertilizers occur in each mixture.

The peak intensity of kaolinite appear to be reduced after 120 minutes of grinding at 600 rpm (Figure 1 A-D). It is noticed that the intensity of the kaolinite bands at 3688 and 3655 cm^{-1} are less than that at 3619 cm^{-1}. Bands of the inner surface hydroxyl groups completely disappear in the mixtures with different ratio of kaolinite and one of the following fertilizers: urea, DAP or KH_2PO_4.

Previous studies reported that the intensity loss of IR peaks is attributed to the degradation of the hydroxyl groups in kaolinite during the mechanochemical process [13-14, 16]. Therefore, the mechanochemical amorphization of kaolinite in our study accounts for the intensity loss of the inner surface hydroxy groups at 3688, 3655 cm^{-1} and the deformation mode at 912 cm^{-1}.

The inner surface hydroxyl band at 3688 cm^{-1}, however, appears in each K_2SO_4 containing kaolinite, and its intensity in the samples with 50-75% kaolinite is higher than in the sample with the 1:3 mass ratio. This suggests that kaolinite partially remained in the crystalline phase.

On the other hand, the major intensity of the K_2SO_4 at ~1100 cm^{-1} and 609 cm^{-1} decreases with the increased amount of kaolinite in the sample (Figure 1 C). When kaolinite content was increased to 75%, the vibration intensities of the fertilizers slightly decrease both in urea and K_2SO_4 (Figure 1 A-C). This indicates that milling results in amorphization of both the kaolinite and the fertilizer [13-15, 17].

At low kaolinite content (25%), Solihin et al. (2011) showed that the amorphous structure is not large enough to incorporate ions from fertilizers, but when the amount of kaolinite is increased, more ions are incorporated into the amorphous structure of kaolin. The ratio of carrier and fertilizer, therefore, is a critical parameter for maintaining high nutrients in a SRF, the less silica added, the better [16].

3.3 The Effect of Milling Speed:

In this part of the study, the mass ratio of (kaolinite : NPK) is fixed at 3:1 and the milling duration of 120 min is used for all the experiments. The milling rotational speed (milling speed) was varied (200, 400 and 700 rpm). All the spectra of kaolinite-NPK mixtures show that the stretching vibration of the hydroxyl groups at 3688 and 3619 cm^{-1} decrease as the milling speed is increased and disappeared from the samples prepared at 700 rpm.

The disappearance of the hydroxyl bending vibration at 912 cm^{-1} and the decrease in the intensity of the Si-O band at ~1000 cm^{-1} also indicate the mechanochemical decomposition of kaolinite at 700 rpm. Band intensities of the studied fertilizers also decrease with increasing the milling speed. These results indicate that higher milling speeds are required to reduce the starting materials to the amorphous phase and allow the incorporation of the nutrients into the kaolinite structure.

According to a previous study [14], a milling process at a minimum of 400 rpm rotational speed is required to incorporate nutrients such as KH_2PO_4 and $NH_4H_2PO_4$ into the amorphous kaolinite structure.

The major contributing factor to the release of nutrients can be the rate of rotation [17]. Our study highlights, that a rotational speed between 400 and 700 rpm would be optimum for the mechanochemical synthesis of kaolinite-NPK fertilizers.

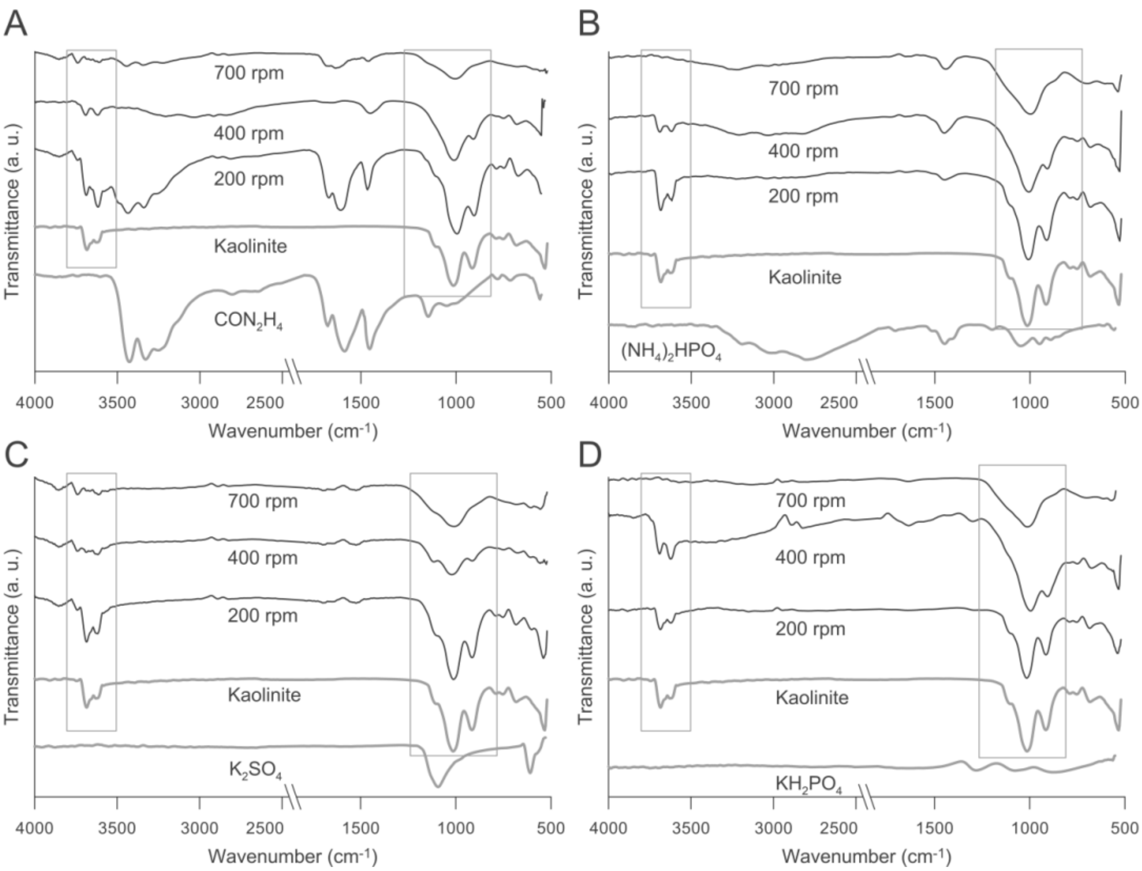

Figure 2. Infrared spectra of kaolinite-NPK mixtures (3:1 ratio) milled at different speeds for 120 min. A: urea, B: DAP, C: K_2SO_4, D: KH_2PO_4.

3.4 The Effect Of Milling Duration:

Figure 3 A-D displays the FTIR spectra of kaolinite-NPK (3:1) mixtures milled at 600 rpm for 60, 120 and 180 min.

The intensities of characteristic bands at 3688, 3655 and 3619 cm^{-1} markedly decrease in each spectrum of the mechanochemically treated samples, indicating the scission of O-H bonds. The weak bands at 3688 and 3619 cm^{-1} indicate that after 60 minutes of milling, some OH groups remained bonded between the adjacent kaolinite layers, evidencing that some residual kaolinite phase still existed. However, on prolonging the milling time up to 120 min, these bands completely disappeared, implying completion of the mechanochemical dehydroxylation process and amorphization.

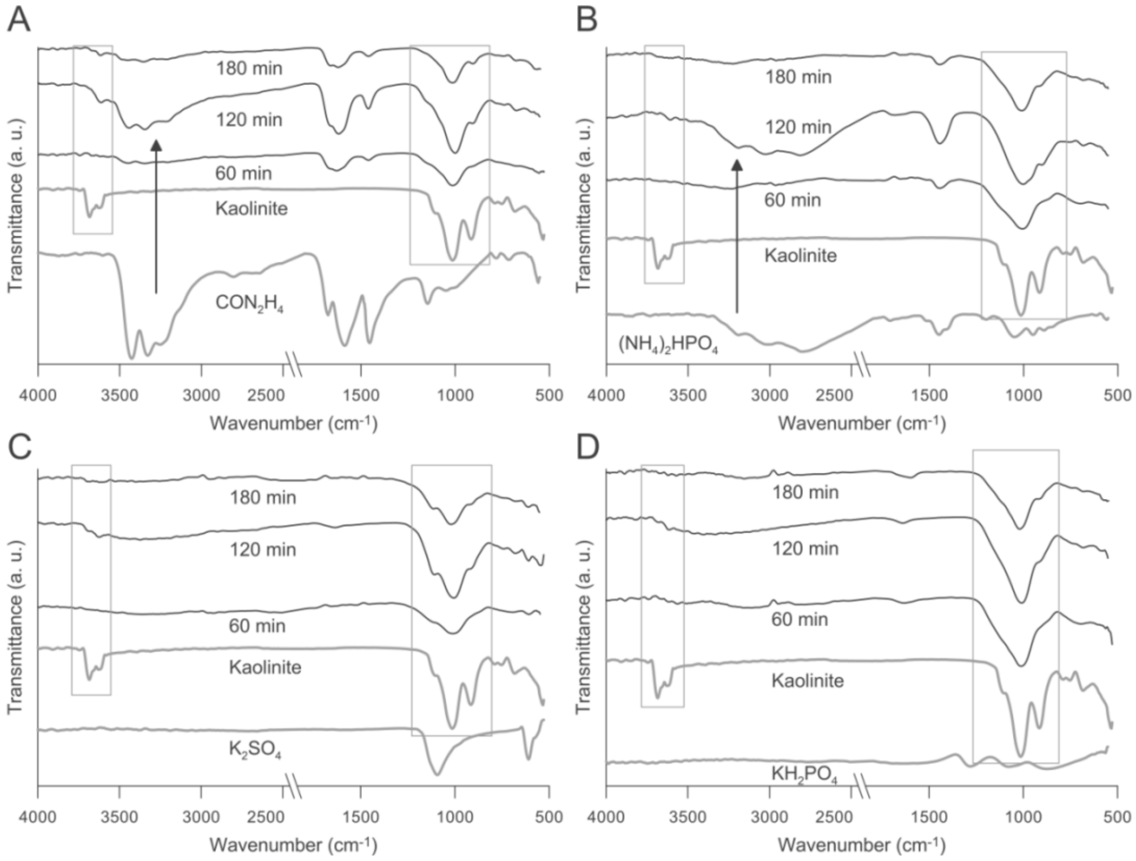

Figure 3. Infrared spectra of kaolinite-NPK mixtures (3:1 ratio) milled at speed 600 rpm for different duration. A: urea, B: DAP, C: K_2SO_4, D: KH_2PO_4.

By comparing intensity of the Si-O band at ~1000 cm^{-1} in the spectra of mixtures after 60 min and 120 min milling, it can be seen that prolonged milling duration strengthens the intensity (Figure 3 A-D). The Si-O stretching vibration increases when the duration of milling reaches 120 min. After 180 min of milling, however, the infrared intensities both of the Si-O network and the fertilizers decrease. Therefore, the incorporation of nutrients into the short order of the Si-O network is complete after 120 min of co-grinding.

Similar results were found in a previous study on urea intercalated kaolinite [24]. Sahnoun et al. (2015) also demonstrated on kaolin-potassium phosphate mixtures that two hours of milling is sufficient to achieve the distortion of the crystalline network of kaolinite in order to insert additive [28].

4. Conclusions

This study investigated the influence of the milling operating parameters (speed and duration) and different mass ratios of kaolinite-NPK mixtures as a slow-release fertilizer using infrared spectroscopy. The selected fertilizers were the most used in agriculture, namely: CON_2H_4, $(NH_4)_2HPO_4$, K_2SO_4, and KH_2PO_4. Incorporation of fertilizers into the structure of kaolinite was successfully carried out by dry co-grinding of kaolinite-NPK mixtures in a planetary ball mill. Infrared spectroscopic results confirmed the mechanochemical dehydroxylation of kaolinite (loss of OH groups), and show that amount of kaolinite, milling speed and milling duration play an important role in the mechanochemical treatment of kaolinite-NPK mixtures. It is recommended to synthesize a slow-release fertilizer with the kaolinite as a carrier to the fertilizer at a mass ratio of 3:1 (kaolinite : fertilizer). The optimum time of milling was found to be 120 minutes at 600 rpm milling speed. Mechanochemical treatment offers an easy access to develop slow-release fertilizers.

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5. References

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