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Mechanochemical Synthesis of Kaolin-Potassium Phosphates Complexes for Application as Slow-Release Fertilizer

Rym Dhouib Sahnoun*, Kamel Chaari and Jamel Bouaziz

Laboratory of Industrial Chemistry, National School of Engineering, University of Sfax, BP 1173, 3038 Sfax, Tunisia

Abstract: In the current study we investigated the effects of the addition of KH_2PO_4, K_2HPO_4 and K_3PO_4 to kaolin by mechanochemical treatment, for the synthesis of new complex compounds. These compounds are offered as slow-release fertilizers. After, the characterization of the ground kaolin, we concluded that two hours of milling is sufficient to achieve the distortion of the crystalline network of kaolin in order to insert additives. The quantity of KH_2PO_4 inserted is not as much as those of K_2HPO_4 and K_3PO_4. This is due to the acid character of those compounds. The amounts of K^+ and PO_4^{3-} released when using KH_2PO_4 are larger than those when using the others additives.

Keywords: Kaolin; Phosphates; Characterization; Fertilizers; Mechanochemical treatment.

Introduction

Fertilizers are the essential input material for the sustainable development of crop production; they play an important role in ensuring food security. However, various environmental and economic drawbacks related to the use of conventional fertilizers became a focus of worldwide concern [1,2]. One way of overcoming these shortcomings involves the use of slow-release fertilizers which have demonstrated many advantages over the conventional types, such as decreasing the rate of fertilizer loss, supplying nutrients sustainably, lowering the frequency of their application, and minimizing the negative effects associated with over-dosage. Coated fertilizers are the major category of slow-release fertilizers [3] which are physically elaborated by coating granules of conventional fertilizers with various materials to reduce their dissolution rate [4-6]. Other types of fertilizers are elaborated through the use of mechanochemical treatment to insert the plant nutrients (potassium, ammonium, nitrate, phosphate), into other structures such as clay. The release rate of nutrients is thus controlled.

Mechanochemistry, term first defined by Ostwald [7] in the late 19th century, is considered as a branch of solid state chemistry dealing with intentional defects in the structure of solid substances by the application of mechanical forces. These defects are often created using intensive milling processes [8, 9]. The formation of defects in solids during intense milling is marked by non-equilibrium conditions. After mechanical treatment, solids became metastable or in an *active* state [10]. The mechanochemical grinding process of a solid has been used to insert other molecules between their layers [11-18].

Kaolin is an important industrial material, used in engineering and construction applications, ceramic processing, environmental remediation and many other diverse applications. There is an ongoing interest in utilizing kaolin clay as a raw material for the manufacture of slow-release fertilizers by intercalating the nutrients in its structure using mechanochemical treatment. Recent studies of the mechanochemical treatment of kaolinite have explained the structural changes which occur upon the grinding of kaolinite [19-22]. It has been shown that the dry grinding of kaolinite along with the inserted molecule increases the degree of intercalation[16-18].

In this paper we characterize the kaolin ground for various times by XRD, FTIR and thermal analysis. In addition we examine the insertion, of potassium dihydrogen phosphate, KH_2PO_4, potassium monohydrogen phosphate K_2HPO_4 and potassium phosphate K_3PO_4 to kaolin by mechanochemical treatment, to obtain a slow-release fertilizers.

Experimental Section

Materials

A high grade kaolin supplied from BWW Minerals is used in the experiments. Its chemical composition in mass% is SiO_2, 52.41, Fe_2O_3, 3.48, Al_2O_3, 29.83, MgO, 0.81; K_2O, 0.73; SO_3, 0.07; CaO, 0.36 with L.O.I at 1000˚C of 12.31.

In this study, the additives used for the synthesis of the new complex compounds are potassium dihydrogen phosphate KH_2PO_4 (Sigma Aldrich,

**Corresponding author: Rym Dhouib Sahnoun*
E-mail address: rymdhouib@yahoo.fr
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density 2.000 g.cm^{-3}), potassium monohydrogen phosphate K_2HPO_4 (Reidel de Haen, density 2.440 g.cm^{-3}) and potassium phosphate K_3PO_4 (Sigma Aldrich, density 2.546 g.cm^{-3}).

Mechano-chemical synthesis

Kaolin and kaolin mixed with different amounts of additives (KH_2PO_4, K_2HPO_4 and K_3PO_4) were ground (mechanochemically activated) using a planetary ball mill (Retsh PM 100). Each milling was carried out with a 100g air-dried sample in a pot having a capacity of 80 cm^3, using stainless-steel balls (10 mm in diameter). The applied rotation speed was 400 rpm.

Characterization

X-ray diffraction (XRD) patterns of the solid samples were obtained using the Philips X'Pert X-ray diffractometer equipment, operating with Cu-Kα radiation (λ= 1.54056 Å). The crystalline phases were identified from the Powder Diffraction Files (PDF) of the International Center for Diffraction Data (ICDD).

The infrared spectra of the samples were recorded in the wavenumber range of 400-4000 cm^{-1}; the spectral resolution was 4 cm^{-1} using a Perkin Elmer Spectrum BX LX 185255 instrument in KBr.

Thermal analysis (DTA and TG) were carried out by using (about) 20 mg of powder (DTA-TG, Seteram Model). The heating rate was 10°C.min^{-1} in a helium atmosphere.

The release of nutrients into water was determined by dissolving 1g of the ground product in 20 ml of distilled water for 24 hours at room temperature. After filtration, the obtained filtrate was determined by a liquid ion chromatography (Shimadzu L10 Series). The results were given in weight percentages.

Results and discussion

Characterization of milled kaolin relative to milling time

X-ray powder diffraction

One means of following the structural alteration resulting from mechanochemical treatment is to use XRD. The XRD patterns of kaolin and kaolin ground for various grinding times are shown in figure 1. As can be seen in this figure, the diffraction patterns for the raw and mechanically treated kaolin are consistent with the quick deterioration of the kaolinite structure during the grinding process. The diffractograms indicate that kaolinite suffers significant structural degradation during the grinding process while the quartz is not altered. After two hours of milling, almost no kaolinite reflections are present in the XRD pattern of kaolin (Figure1). The loss of intensity and the relative area in the peak at 0.71 nm (2θ = 12.4°), which increased with grinding time, suggest the breaking of the bonds between kaolinite layers (001) (Figure 1). This means the demolition of the kaolinite structure happened because of the distortion and breakage of the crystalline network. We note also the fast deterioration of the kaolinite structure during the milling process, especially within the first 15 minutes. The XRD patterns indicate that the quartz phase has not been altered because the position of peaks at 21.2° and 27.4° remains almost unchanged. This non-altered quartz content caused the acceleration of the mechanochemical activation of the kaolinite. We believe that the harder quartz grains act as additional grinding bodies during the dry grinding of kaolin [23].

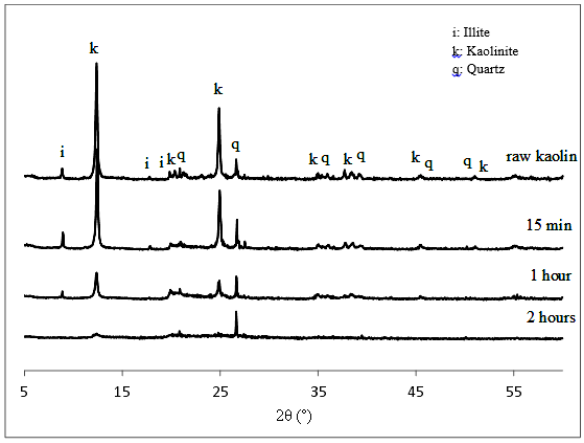

Figure 1. XRD spectra (Cu Kα) of kaolin milled for various grinding times.

FTIR spectrometry

Figure 2 shows the FTIR spectra of the kaolin clay in comparison to those of kaolin clay ground for 15 min, 1 h and 2 h, observing this figure, three regions are noted:

- ***Hydroxyl-stretching mode:*** This region is where most of the changes occur due to grinding. From the spectra we conclude:
- The intensity of all the hydroxyl stretching vibrations decreases with grinding time,
- The intensity of the bands attributed to the inner surface hydroxyl decrease faster than the band of the inner hydroxyl which means that the inner surface hydroxyls are lost before the inner hydroxyls,
- The out-of-phase behavior is removed by the mechanochemical treatment,

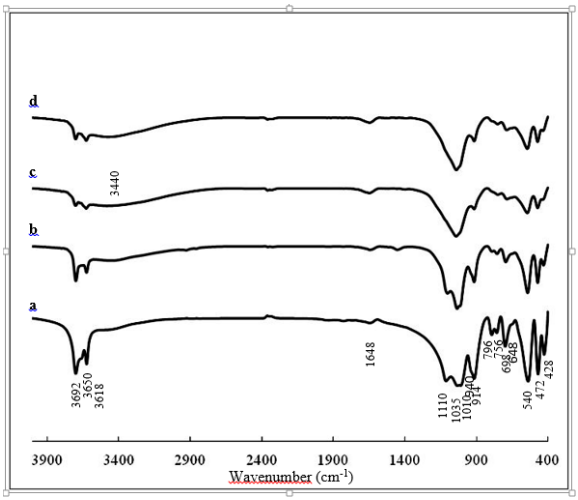

Figure 2. IR spectra of kaolin milled for various grinding times: a: raw kaolin; b: 15min; c: 1h; d: 2h.

- ***Hydroxyl deformation mode****:* Two bands are observed. First one at around 940 cm^{-1} is attributed to the hydroxyl deformation mode of the inner surface hydroxyl. Second one at around 914 cm^{-1} is ascribed to the hydroxyl deformation mode of the inner hydroxyl. In harmony with the loss of intensity of the hydroxyl-stretching vibrations, a decrease in intensity of the hydroxyl-deformation modes is observed. We note the decrease in intensity of those bands with the increase of grinding time. In fact after 15 min of grinding no intensity remains. Therefore, we conclude that the Inner surface hydroxyls are removed, by mechanochemical treatment, before the inner hydroxyls.

- ***Silicon-oxygen vibrations****:* In order to study the low wavenumber region of mechanochemically treated kaolinites, it is convenient to divide the spectra into two sections: (a) the SiO stretching vibrations and (b) the OSiO bending region. Band component analysis of the region 970 to 1170 cm^{-1} shows the presence of three bands in the IR spectra of the ground kaolin at 1110, 1035, and 1010 cm^{-1}. The spectral profile of this region shows a steady decrease in intensity with mechanochemical treatment and the bands appear to broaden at the same time. The band at 1010 cm^{-1} remains constant in position and intensity; however the bands at 1035 and 1110 cm^{-1} display changes in intensity with mechanochemical treatment. The intensities of those bands decrease with the increase of grinding time until they disappear. It is proposed that as the time of grinding increases, the hydroxyls are removed and the surface becomes similar to an alumina or siloxane surface.

The low-wavenumber region between 400 and 900 cm^{-1} may be divided into two parts: (a) the region from 650 to 850 cm^{-1} and (b) the region from 400 to 650 cm^{-1}. The first region shows the spectra of the hydroxyl translation modes and reflects changes in the SiO chains as the hydroxyl unit moves in and away from the siloxane chain. Bands are observed at 796, 756, 698 and 648 cm^{-1}. These bands reflect the degree of defect in the kaolinite stucture. As with all the other bands in the spectra of the kaolin, the bands decrease in intensity with mechanochemical treatment. After 1 h of grinding, little intensity remains. The second part of the spectra is attributed to OSiO and SiOAl vibrations. Bands are observed at 540, 472 and 428 cm^{-1}. The variation in intensity of these bands appears to decrease with mechanochemical treatment.

Thermal analysis

The DTA pattern for the natural sample (Figure 3) exhibits two peaks. The first is an endothermic one at 515 °C associated with the loss of hydroxyl groups from the kaolinite structure and the formation of a metakaolin phase. The second peak is an exothermic one at 998 °C attributed to the formation of a spinel and/or crystal mullite phases. The destruction of the kaolinite structure by the distortion and breakage of the crystalline network caused by milling, as mentioned above, was confirmed by the DTA analyses (Figure 3). Subsequently, the temperature and the area of the endothermic peak (515°C) decrease with the increase of grinding time. Furthermore, after 2 h of grinding, this transformation almost disappears. These changes in the endothermic peak can be attributed to a reduction in the amount of heat required to break the structure of kaolinite. The latest may be destroyed before by mechanical treatment. This fact suggests that the hydroxyl groups are reduced in number and are more weakly bonded [28]. The dehydroxylation process is preceded by a dehydration step spanning the temperature range of 80-120 °C, where a small amount of water is detected in the case of the raw kaolin. However, we note an increase of the area of the broad peak assigned to the dehydration process for the ground kaolin. Then, we conclude that almost the whole quantity of hydroxyl groups is eliminated in the mechanical dehydroxylation step, especially in the case of the kaolin ground for 2 h.

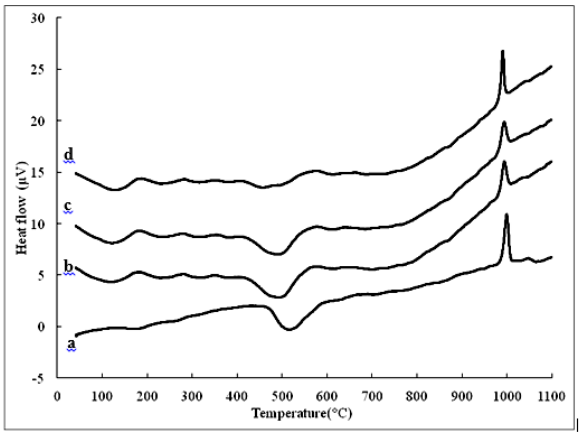

Figure 3. DTA curves of kaolin milled for various grinding times: a: raw kaolin; b: 15min; c: 1h; d: 2h.

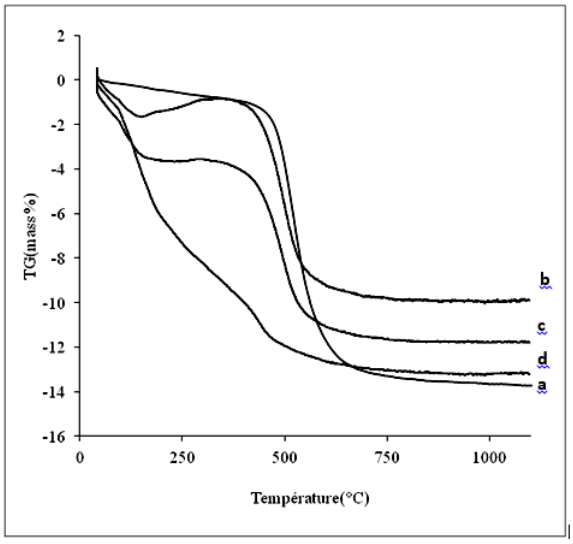

Figure 4. TG curves of kaolin milled for various grinding times: a: raw kaolin; b: 15min; c: 1h; d: 2h.

The thermogravimetric analysis of kaolin shows the biggest weight loss at 400-700°C due to the destruction of the kaolinite structure caused by its

dehydroxylation (Figure 4). However, the TG curves of the mechanically treated kaolin exhibit two steps. The first step, between 40 and 250°C, can be assigned to the release of water formed through mechanical dehydroxylation of kaolinite. The second, above 400°C, is caused by the loss of water in the thermal dehydroxylation process [28]. As can be seen in figure 4, the first and second weight loss vary with the milling time. Therefore, a progressive increase of the weight loss in the low temperature range occurs relative to the milling time. The fact that the second weight loss decreased with the milling time suggests that the structure was partially destroyed and that the hydroxyl groups were more weakly bonded. This indicates that the decrease of the weight loss in the high temperature ranges is attributed to an anticipation of dehydroxylation towards low temperatures. This fact is a consequence of an increase of defects in the octahedral structure which is due to the progressive milling time [29, 30].

It seems that after the characterization of the ground kaolin, two hours of milling is enough to achieve the distortion and breakage of the crystalline network of kaolin in order to insert additives such as KH_2PO_4, K_2HPO_4 and K_3PO_4 for the synthesis of slow-release fertilizers.

Characterization of the mixtures kaolin-potassium phosphates (XRD and IR)

To study the insertion of phosphate and potassium in the network of kaolin to be used as slow-release fertilizers, the mixtures of kaolin-KH_2PO_4, K_2HPO_4 or K_3PO_4 in different proportions were ground for 2 h.

Figure 5 shows the XRD patterns of the kaolin-KH_2PO_4 mixtures prepared with different amounts of KH_2PO_4. As it can be noticed, the XRD patterns of the mixtures prepared with 25 mass% and 35 mass% of KH_2PO_4 contain almost only the characteristic peaks corresponding to the quartz. However, the peaks attributed to KH_2PO_4 start to appear only when its quantity in the mixtures exceeds 55 mass%.

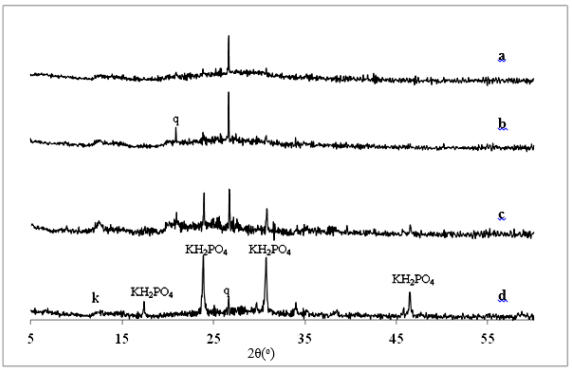

Figure 5. XRD patterns of kaolin-KH_2PO_4 sample system with varying amounts of KH_2PO_4 (mass %) milled for 2h at 400 rpm a: 25 mass%; b: 35 mass%; c: 55 mass% and d:75 mass%.

The figure 6 reports the IR spectra of raw kaolin and kaolin-KH_2PO_4 sample system with varying amounts of KH_2PO_4 (mass %) milled for 2h at 400 rpm. While observing figure 6, we note the following conclusions:

a-A further decrease in intensity until the total disappearance of the 3692 cm^{-1} band is observed. This is expected as the intercalation results from the hydrogen bonding with the phosphate of the inner surface hydroxyls of kaolinite;

b-The increase of the amount of KH_2PO_4 causes the decrease of the intensity of the 3618 cm^{-1} band;

c-A broad band attributed to the adsorption of water appears at 3270 cm^{-1};

d-The broadening of the band at 1040 cm^{-1} is assigned to the SiO stretching mode. This change is also due to the existence of a new vibration band of PO from KH_2PO_4.

e-The characteristic bands of KH_2PO_4 (2440, 1730, 1300 and 890 cm^{-1}) begin to appear when the addition of KH_2PO_4 reaches 55 mass%.

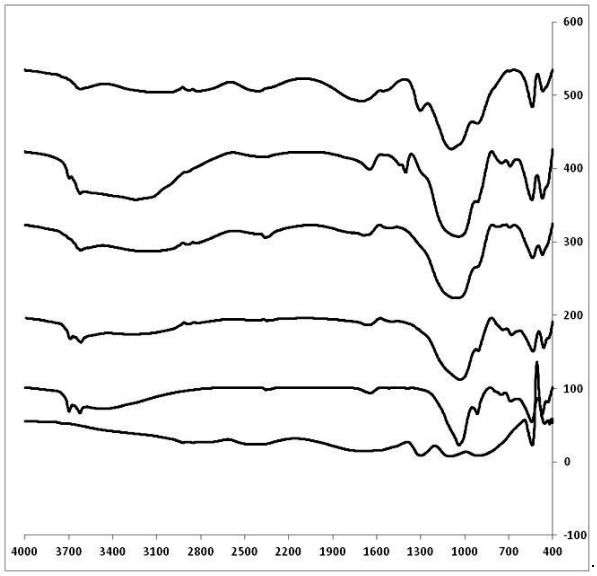

Figure 6. IR spectra of raw kaolin and kaolin-KH_2PO_4 sample system with varying amounts of KH_2PO_4 (mass %) milled for 2h at 400 rpm.

As a result from the IR and XRD analyses, we conclude that KH_2PO_4 is intercalated in the structure of kaolin to the point where its quantity is under 55 mass%. This means that at a low content of kaolin, the distorted crystal of kaolinite was not large enough to receive all the K^+ and PO_4^{3-} atoms from the starting material. However when the content of kaolin increased, the capacity of kaolin to receive KH_2PO_4 improved. Thus all K^+ and PO_4^{3-} atoms were incorporated into the structure of kaolin.

Characterization by XRD and IR analyses of the kaolin-K_2HPO_4 sample mixtures with varying K_2HPO_4 contents (mass %) ground for 120 minutes is shown in figures 7 and 8. With the addition of 25 mass% of kaolin, clear peaks corresponding to K_2HPO_4 remain in the milled product. When the quantity of kaolin increases to 35 mass% both starting samples were reduced to a state of poor diffraction.

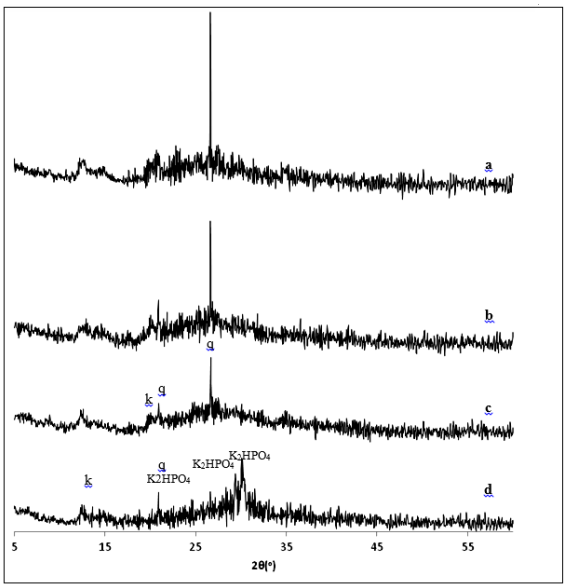

Figure 7. XRD patterns of kaolin-K_2HPO_4 sample system with varying amounts of K_2HPO_4 (mass%) milled for 2h at 400 rpm. a: 25 mass%; b:35 mass%; c:55 mass% and d:75 mass%.

By observing the IR spectra illustrated in figure 8, we note the presence of the broad band centered at 3400 cm^{-1}, indicating the hydrogen bonding, while the characteristic bands of K_2HPO_4 appear in the IR spectrum of the complex kaolin-75 mass% K_2HPO_4. This means that at low kaolin content, and as discussed in the case of the kaolin-KH_2PO_4 sample, the amorphous structure was not large enough to incorporate K^+ and PO_4^{3-} Thus, we note that a quantity between 55 mass% and 75 mass% of K_2HPO_4 can be intercalated in the network of the kaolin.

The same results were obtained in the case of the kaolin-K_3PO_4 mixtures. This is well represented in figures 9 and 10 supporting this conclusion. In fact, modification of the XRD and IR patterns of the mixtures is noted only when the quantities of added K_3PO_4 reach 75 mass%.

The quantity of KH_2PO_4 included in the structure of kaolin is not equal to those of K_2HPO_4 and K_3PO_4. This is probably due to the acid character of those compounds. Also, we believe that the alumina octahedral layer in the structure of kaolinite protonated to form the surface of the complex $AlOH^{2+}$ with a positive charge; meanwhile, the silica tetrahedral layer in the structure of kaolinite deprotonated to form the complex SiO^- with a negative charge. Consequently, two adjacent layers in the kaolinite are held together by electrostatic forces, which is not favorable to intercalation. As a result of this hypothesis, the amounts of the intercalated K_3PO_4 and K_2HPO_4 are higher than that of KH_2PO_4 which has a greater acidic character than that of the other phosphates.

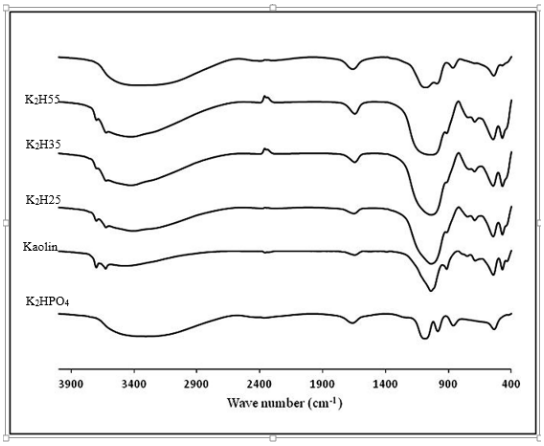

Figure 8. IR spectra of raw kaolin and kaolin-K_2HPO_4 sample system with varying amounts of K_2HPO_4 (mass%) milled for 2h at 400 rpm.

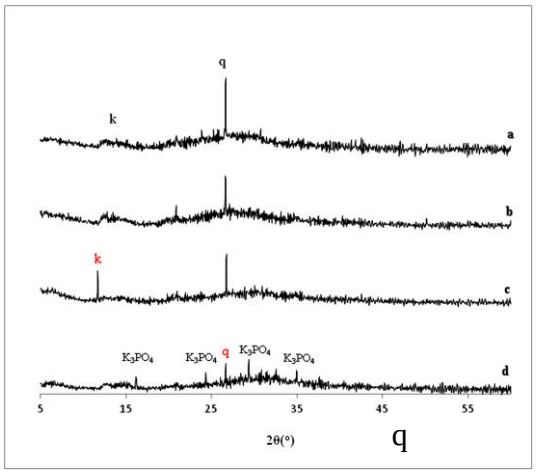

Figure 9. XRD patterns of kaolin-K_3PO_4 sample system with varying amounts of K_3PO_4 (mass%) milled for 2h at 400 rpm (a: 25 mass%; b:35 mass%; c:55 mass% and d:75 mass%).

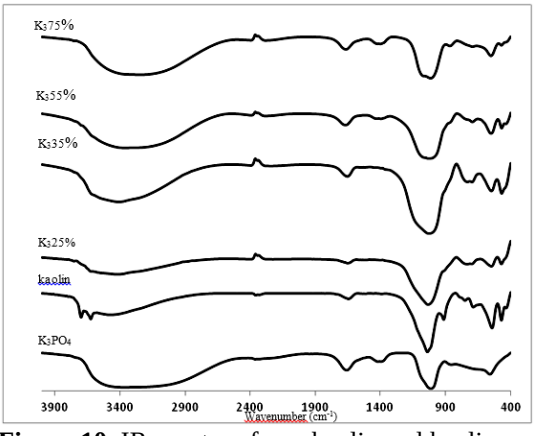

Figure 10. IR spectra of raw kaolin and kaolin-K_3PO_4 sample system with varying amounts of K_3PO_4 (mass%) milled for 2h at 400 rpm.

The behavior of the release of nutrients

The main purpose of this work is to develop the kaolin-KH_2PO_4, K_2HPO_4 or K_3PO_4 complexes used as

slow-release fertilizers. This implies that the slower the release of K and P, the better the performance of the fertilizers. Figures 11 and 12 illustrate the following points:

1- The release rate of the nutrients decreases when the content of kaolin increases.

2- For all complexes, the released quantities of K and P are higher than those in the case of the mixtures with 25 mass% of kaolin. This can be explained by the fact that, and as mentioned in the previous section, when the content of kaolin is 25 mass%, the capacity of the distorted structure of amorphous kaolin to incorporate the phosphate additives is insufficient and the excess of KH_2PO_4, K_2HPO_4 or K_3PO_4 in the milled mixtures readily dissolves when dispersed in water.

3- Sufficient kaolin content in the mixtures increases its capacity to allow the incorporation of KH_2PO_4, K_2HPO_4 or K_3PO_4 into the amorphous structure. When dispersed in water, the $PO_4^{3-}$and K^+ ions could not readily pass through the kaolinite structure or network before dissolving into water, resulting in the sharp decrease of the rate of the release of nutrients.

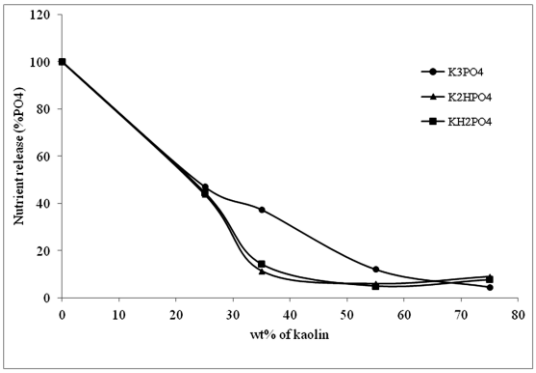

Figure 11. Nutrients release profile of PO_4^{3-} kaolin-potassium phosphates samples system with varying amounts of kaolin (mass%) milled for 2h at 400 rpm.

4- The amounts of K^+ and PO_4^{3-} released when using KH_2PO_4 are higher than those when using the other additives. We believe that this occurs in connection with the rate of the incorporated amount of each additive.

5- The liberation of potassium is easier than that of phosphate because potassium is smaller.

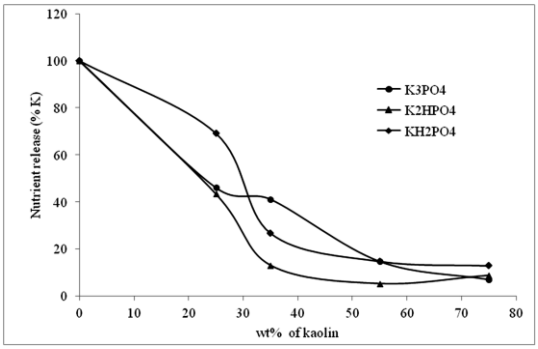

Figure 12. Nutrients release profile of K^+ kaolin-potassium phosphates samples system with varying amounts of kaolin (mass%) milled for 2h at 400 rpm.

Conclusion

The insertion of K^+ and PO_4^{3-} ions as plant nutrients from KH_2PO_4, K_2HPO_4 or K_3PO_4 compounds into the structure of kaolin, through mechanochemical treatment, was successfully reached. The results in the current work can be summarized as follows:

a- It seems that two hours of milling is sufficient to achieve the distortion and breakage of the crystalline network of kaolin.

b-The quantity of KH_2PO_4 introduced in the structure of kaolin is smaller than those of K_2HPO_4 and K_3PO_4. This is probably due to the acid character of those compounds.

c- The release rate of the nutrients decreases when kaolin content increases.

d- The amounts of K^+ and PO_4^{3-} released when using KH_2PO_4 are higher than those when using the other additives. We believe that this occurs in connection with the rate of the incorporated amount of each additive.

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