Physio-Chemical Preparation of Slow-Release Potassium Fertilizers

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Abstract

Background: In this work, one of the novel types of slow-release fertilizers (SRF) consisting of kaolin as clay material and K_2SO_4 was synthesized through a mechanochemical process by grinding in a ball mill planetary model.

Methodology: The test samples of different weight % from 25 to 75 of kaolin contents were milled for 2 h at fixed milling speeds of about 600 rpm to assess the integration of K_2SO_4 and to measure the liberation of K^+ and SO_4^{2-} ions into solution. The properties of the studied samples were characterized by Fourier transformation infrared spectrometry (FTIR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and ion chromatography (IC). Incorporating K_2SO_4 into an amorphous kaolin structure using mechanochemistry is a green chemistry method that has been successfully applied. K^+ content was measured in deionized water solution and the soil column leaching test was performed to determine the slow-release performance of the material.

Results: The optimum released amount of K^+ after 24 h was for (1:1 wt ratio) kaolin - K_2SO_4 samples that were 123.9 ppm at milling conditions at 600 rpm milling speed for 2 h.

Conclusion: Indicating that K_2SO_4 – kaolin milled samples has good slow-release properties under specific conditions. In addition to being cost-effective and eco-environmentally, with prepared SRF, we can significantly increase the efficiency of fertilizer utilization in green agriculture.

Keywords: kaolin, mechanochemical milling, Corporation, Slow release, Physio-chemical.

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1. Introduction:

Modern agriculture relies heavily on potassium as a nutrient for plant growth (1). Most potassium is obtained from the evaporation of clays such as Kaolin, Feldspar, Ddickite, Chrysotile, and other minerals that are abundant on earth but highly dispersed. It affects the sustainable development of local agriculture when soils lack potassium in many parts of the world. Meanwhile, potassium is present in many mineral solids like mica, alunite, and K-feldspar that are unavailable to utilize due to their water-insoluble nature. It may greatly enhance security for the stability of agriculture If potassium can be sourced from these unexamined sources in a balanced manner (2).

Water eutrophication and nutrient loss from floods or permeation of a current chemical fertilizer that is highly soluble are common problems in rainy climates (1), (3). These problems result in increased farming costs and nutrient loss of fertilizer in water (4). It has been widely accepted that slow-release fertilizer (SRF) can overcome some of these challenges. Several techniques are used to make commercial SRF, including coating fertilizer particles with polymers. Regardless, a novel approach to activating undeveloped minerals to produce SRF products has been proposed (2), (4), (5). Chemical and material industries have been pursuing solvent-free mechanochemical processes (6)–(9).

Researchers have extensively reported mechanochemically induced solid-state reactions to produce SRF by ball milling kaolin or Al_2O_3 with soluble sodium, potassium, or phosphorus salts (7), (8), (10). The starting samples in these cases must however be potassium/ammonium phosphate chemical salts, which are still based on today's fertilizer production (11). Its obvious benefits, including cost reduction and environmental friendliness, are evident when natural minerals are transformed directly into SRF (12).

Many crop production systems do not give as much attention to potassium as nitrogen and phosphorous, but potassium is an essential nutrient for plant growth. Regardless of nutrient management philosophy, K is recognized as the soil cation required by plants in the greatest amount (13), (14).

A potential solution to alleviate such problems and increase nutrient utilization efficiency could be slow-release fertilizers (SRFs). This reduces the loss of nutrients since SRFs gradually release nutrients according to the specific requirements of a plant (15), (16). SRF offers several advantages over conventional fertilizers. These include a higher nutrient efficiency, continuous and predictable supply of nutrients for a long period, and a lower amount of nutrients lost to volatilization and leaching (9), (13).

A lot of industrial applications have been demonstrated with clay materials in some recent studies. The micronized mixtures of kaolin with KH_2PO_4 or $(NH_4)_2HPO_4$ were prepared by (14) by grinding in a planetary ball mill. Using a mechanochemical process, the researcher created amorphous Kaolin, which is a carrier for nutrients including K^+, NH_4^+, and PO_4^{3-} that can be slowly released as fertilizer (7). As slow-release fertilizers derived from glauconite, the complex is mechanochemically synthesized by (6).

The objective of this study is to investigate the effect of milling conditions on the properties of the kaolin–K_2SO_4 system by reducing the kaolin clay mineral to an amorphous phase and chemically bonding K–Al–Si–P–O with water to obtain an amorphous glass phase. The long-term target product will eventually be a water-insoluble matrix that will act as an SRF fertilizer by combining K^+ and SO_4^{2-} nutrients in a regulated manner. To obtain green agriculture chemistry products with desired properties, different milling conditions were investigated for fixed kaolin contents.

2. Experimental:

2.1 Materials and Methodology

The kaolin ($Al_2Si_2O_5(OH)_4$) (> 90% purity) was gated from Jordan- Wadi Araba region (17), (18), and the potassium sulfate (K_2SO_4) was obtained from Merck. Kaolin was ground with K_2SO_4 and Pulverisette-7 (Germany) planetary ball mill under dry conditions to prepare samples. There were two zirconia mill pots (45 cm^3) containing six zirconium balls each 15 mm in diameter in the planetary ball mill. The experiment in Table (1) presents the results of the application of milling time and speed on the release of nutrients from Kaolin with K_2SO_4 at a fixed milling time.

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Table (1): The ratios and conditions of mixtures used in the experiments

(Kaolin- K_2SO_4)	Milling speed (rpm)	Milling time (min)
	Weight ratio	
1:3, 1:1, 3:1	600	120

To prevent excessive heat during milling, five minutes of rest between milling operations were incorporated into all experiments.

2.2. Characterization

Fourier transformation infrared spectra were collected from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1} using an EPS-870 spectrometer (NEXUS). The x-ray diffraction patterns of a Cu tube were analyzed first before and then after milling on a Philips PW-1710 automated diffractometer at a voltage and current of 40 kV and 30 mA, counting for two seconds in each step. An analysis of thermal properties from room temperature to 1000°C was performed using differential thermal analysis (TG-DTA; STA-409 PC; NETZSCH) in an atmosphere of N_2.

In this work, nutrient release behavior from a synthesized mixture was examined. During the soil column leaching experiments in distilled water, In a 100 mL glass beaker, 1 g of milled plant material was combined with 20 mL of deionized water. The sample was soaked in the solution for 24 hours. The separation of solids and liquids was performed by suction filtration on filter papers with pore sizes of 0.45 μm. IC (Chemical Analysis, Column: Series Dionex CS-5000+DP, Germany) was utilized to conduct the concentrations of K^+ and SO_4^{2-} nutrients released.

3. Results :

Potassium sulfate is considered a good soluble fertilizer and a source for K^+ and SO_4^{2-} ions in the soil. Since nutrients are released at a slower rate throughout the season, slow-release fertilizers are excellent alternatives to soluble fertilizers where plants can absorb most of the nutrients without much loss by leaching. This section focuses on the efficiency of different parameters in releasing K^+ and SO_4^{2-} from K_2SO_4.

3.1 Mechanochemical Synthesis of Kaolin and K2SO4 Based on Material Weight Percentage

In this section, we consider the influence of raw material weight ratios on the integration of the kaolin–K_2SO_4 sample mixture. During all runs, milling time was set at 120 minutes and rotational speed was set at 600 pm.

The FTIR spectra shown in Figure 1 indicate that chemical reactions did not occur at low rotation in the high-energy ball mill. The spectra of these samples show only an overlap relating to the physical mixture of the reactants.

The IR bands of K_2SO_4 that appeared at ~ 609 and 1100 cm^{-1} are assigned to the bending and stretching of the SO_4 groups (9), (19).

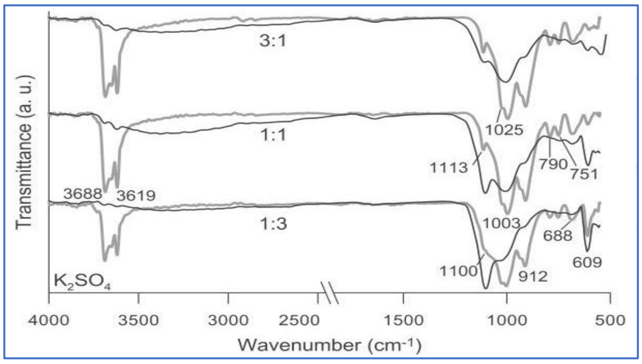

Figure (1): The FTIR spectrum of Kaolin-K2SO4 sample mixtures (light face) and (boldface) samples was milled at 600 rpm for 120 minutes according to different weight ratios (20).

Interestingly, the samples (25 %, 50 %, and 75 %) showed dehydroxylation of Kaolin contributing to the amorphization as the characteristic inner surface hydroxyl bands (3688-3619 cm^{-1}), and internal hydroxyl bands (3619 cm^{-1}) were missing. Water molecules are formed by proton transfer during the mechanical dehydroxylation process, as indicated in the commonly accepted theory (9), (20). In the K_2SO_4 spectrum at (1101 cm^{-1}), there is now a clear band moving upfield in various samples but is almost gone in the Kaolin 75 % sample, which signifies complete intercalation of K_2SO_4. Moreover, for all samples, distinct broad bands were observed for the region around 1000 cm^{-1}, which is attributed to the overlap of Al-OH, Si-O, and P-O vibrations.

Based on the XRD pattern Figure (2), the corresponding characteristic patterns of kaolin and K_2SO_4 have absent from the products, suggesting that K_2SO_4 may have become part of the amorphous structure.

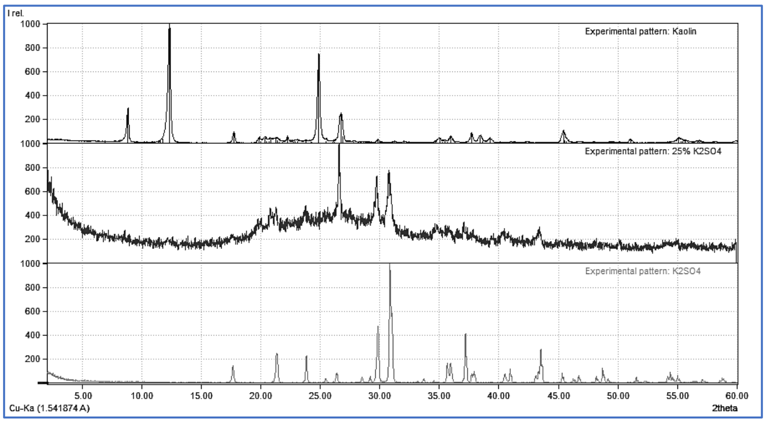

Figure (2): XRD patterns of kaolin–K_2SO_4 system milled at 600 rpm for 120 minutes with various amounts of kaolin present.

As shown in Figure (3), a mass loss of 12.3 % was measured from thermal dehydroxylation of the kaolin agreed well with the expected value of 13.96 %. This indicates that the used kaolin is of high quality. There was no decomposition of the sulfate salts. As observed by XRD and FTIR patterns, the observed behavior is consistent with the formation of amorphous phases from the mixture of the reagents. As a result of grinding, no mass loss of the starting materials is observed in the potassium sulfate samples, indicating that the materials were destroyed during the grinding process.

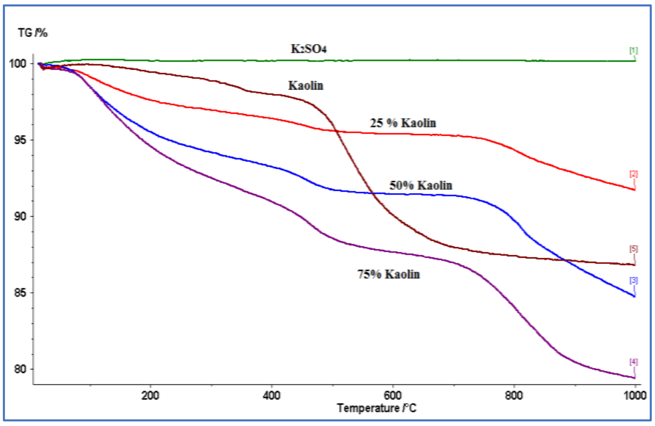

Figure (3): TGA patterns for kaolin and K_2SO_4 mixtures were ground for 2 h at 600 rpm.

Figure (3) also shows that the (75 % Kaolin: 25 % K_2SO_4) sample had a larger mass loss event than the (50%:50%) and (25%:75%) samples, The results showed that when kaolin content is increased in the sample, A new material is formed by mechanochemical reactions, which incorporates K^+ from K_2SO_4 into Kaolin's amorphous structure.

4. Discussion:

Based on milling the kaolin–K_2SO_4 sample mixtures at 600 rpm for 2 h, the following concentrations of K^+ and SO_4^{2-} nutrients were measured (14).

Table (2): K^+ and SO_4^{2-} nutrients were released at different weight ratios when milling Kaolin-K_2SO_4 samples at 600 rpm for 120 min.

kaolin Percent Weight	K^+ Conc. (ppm)	SO_4^{2-} Conc. (ppm)
25	794.0	3077.7
50	123.9	2892.1
75	34.2	2747.7

According to Table (2), A release of nutrients occurs from Kaolin-K_2SO_4 at a slower rate when kaolin content increases. During the sample preparation process, the milling time was kept constant at 120 minutes, and the rotational speed was at 600 rpm.

In the kaolin-K_2SO_4 system, the K+ nutrient migration profiles were determined as a function of volumetric kaolin content (wt. %). Figure 4 illustrates that nutrients are released at a slower rate when the kaolin content is increased.

With the addition of 25 wt. % of kaolin, nutrients such as K^+ and SO_4^{2-} were present in quantities of 794 and 3077.7 ppm, respectively. However, when adding 50wt. % kaolin, the K^+ nutrients released were sharply depleted to 124 ppm while SO_4^{2-} nutrients were slightly reduced. As a result, Kaolin held more K^+ and SO_4^{2-} ions. As the weight percent of kaolin mineral in the prepared mixture was raised to 75 wt. %. In contrast, the amount of K^+ nutrients released decreased dramatically to 34.2 ppm. This is the result of kaolin being 25 weight %.

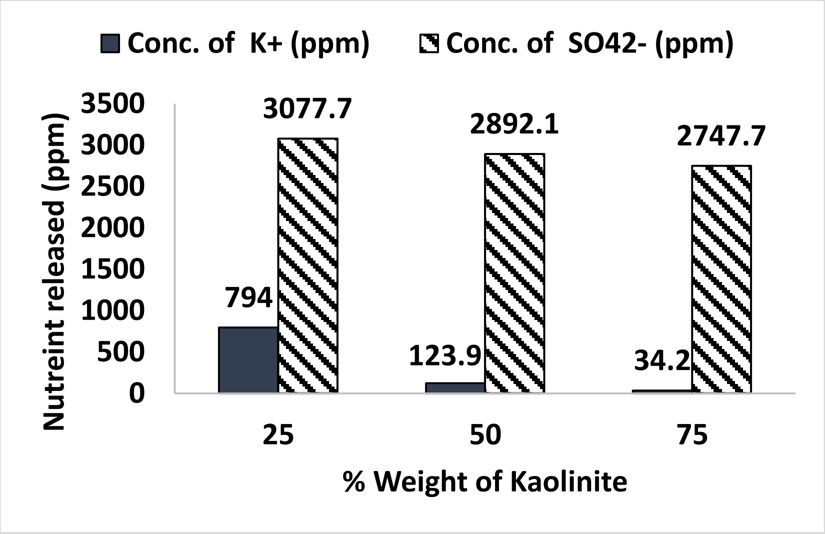

Figure (4): An analysis of the nutrients released from Kaolin–K_2SO_4 samples milled for 120 minutes at 600 rpm with varying amounts of Kaolin (wt%).

An excess of salts in the milled mixture easily disperses in water because amorphous kaolin is not able to incorporate as much K_2SO_4 as pure kaolin can. As a result of the adequate kaolin amount in the sample mixture, the prepared mixture was able to retain more K_2SO_4 in its structure. The kaolin structure or network could not readily permit K^+ ions to pass through before dissolving into the water after dispersion, resulting in sharply reduced nutrient release.

5. Conclusions:

Our results confirmed that new mixtures of Kaolin– K_2SO_4 can act as a slow-release fertilizer as a green chemistry production of fertilizers in the agriculture field. Hence, the mechanochemical process is successfully used to synthesize a novel SRF through the integration of K^+, and SO_4^{2-} ions as plant nutrients from K_2SO_4 into the amorphous structure of kaolin as a clay mineral. The speed and time of milling for raw materials assumed a significant role in the solid-state mechanochemical synthesis as an eco-sustainable process.

6. Acknowledgment:

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7. Conflicts of interests:

The authors declare no conflict of interest.

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التحضير الفيزيوكيميائي لأسمدة البوتاسيوم ذات التفكك البطيء

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الخلاصة

خلفية البحث: تتناول هذه الورقة البحثية تحضير أحد الأنواع الجديدة من الأسمدة ذات التفكك البطيء (SRF)التي تتكون من الكاولين كمادة طينية و K_2SO_4 باستخدام طريقة التفاعل الميكانوكيميائي حيث يتم الطحن باستخدام مطحنة الكواكب الكروية.

طريقة العمل: تم طحن عينات ذات نسب وزنية مختلفة تتراوح بين 25 ٪ إلى 75 من معدن الكاولين لمدة ساعتين و بسرعة طحن ثابتة تبلغ حوالي 600 دورة في الدقيقة لتقييم ترابط K_2SO_4 مع الكاولين، وقياس عملية انطلاق أيونات K^+ و $SO4^{-2}$ في المحلول . وتم دراسة خصائص العينات بمقياس أطياف الأشعة تحت الحمراء(FTIR) ، وحيود الأشعة السينية (XRD) ، والتحليل الوزني الحراري (TGA)، وكروماتوغرافيا الأيونات .(IC) لدراسة اندماج K_2SO_4 في بنية الكاولين غير المتبلورة باستخدام الكيمياء الميكانيكية .كما تم دراسة محتوى K^+ في محلول مائي منزوع الأيونات وإجراء اختبار ترشيح عمود التربة لتحديد أداء التفكك البطيء للمادة .

مناقشة النتائج: كانت الكمية المثلى التي تم إطلاقها من K^+ بعد 24 ساعة لعينات الكاولين-K_2SO_4 (1: 1 wt) التي كانت 123.9 جزء في المليون في ظروف الطحن 600 دورة في الدقيقة سرعة الطحن لمدة 2 ساعة.

الخلاصة: تشير النتائج إلى أن عينات K_2SO_4 - الكاولين المطحونة ذات خصائص جيدة وبطيئة التفكك والاطلاق في ظروف محددة . بالإضافة إلى كونها طريقة فعالة وغير مكلفة من وآمنة بيئيا، وبالتالي يمكننا زيادة كفاءة استخدام هذا النوع من الأسمدة في الزراعة الخضراء بشكل كبير.

الكلمات المفتاحية: الكاولين، الطحن الميكانوكيميائي، الإرتباط، التفكك البطيء، الفيزيويكيميائي.

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