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Simple Approach in Measuring the Synthesized Zeolite from Kaolin as Nutrient Retention for Mung Bean Growth

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Abstract: Since the 1960s, zeolites mesoporous structures have been employed in agriculture due to their efficiency as soil modifiers for plant growth that can retail minerals and important nutrients as well as cation exchange capacity (CEC). This characteristic is critical in ensuring that plant growth is not hampered by the elimination of minerals and nutrients from the fertilizer; thus, zeolite materials are always referred to as slow-release or slow retention of fertilizer. The purpose of this study is to evaluate the performance of kaolin-synthesized zeolites as controlled release fertilizers to reduce soil nutrient leaching. The zeolite Linde-type A used in this study was produced by hydrothermal synthesis from metakaolin clay (thermal treatment). This study's metakaolin clay was made through thermal treatment (calcination) of kaolin clay heated at 650 °C for 24 hours. X-ray diffraction (XRD) was used to determine that the phase of the synthesized zeolite was of the LTA type. An experiment is conducted to examine the effects of zeolite on the trapping and sustaining of NPK fertilizer for plant growth. Compared to standard NPK fertilizers without zeolite, the fertilizer containing zeolite accelerated the growth of mung bean plants by 35.5% for stem height and 52.5% for leaf length. This study indicated that zeolite has a strong capability for retaining minerals and nutrients, guaranteeing that plant growth is not inhibited by nutrient deficiency.

Keywords: Zeolite, kaolin, hydrothermal, mung bean

1. Introduction

Nutrient leaching from soil varies based on the type of soil properties and rainfall intensity. Moreover, nutrient losses through leaching are generally higher in humid climates than in dry climates [1], [2]. Macropores are large soil pores that flows water under there is heavy rainfall or irrigation; otherwise, they are filled with air [2]. Furthermore, because a solution with a high nutrient concentration will infiltrate rapidly into the soil with little contact with the composition of the solid phase (soil matrix), soil system structure macropores and loosely compact easily generate

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fertilizer leaching [3]. Nutrient leaching also occurs in soils with high water infiltration rates and low nutrient retention capacity, such as sandy soils and well-structured ferralitic soils with low-activity clays and low organic matter that will create a deficiency of nutrients indirectly and will disrupt plant growth [4]. There were many deficiencies in nutrients and yield of crops before farmers were introduced to fertilizers [5], [6]. Therefore, to overcome this problem, important nutrients such as nitrogen, phosphorus, and potassium were introduced in fertilizer. The availability of industrial-made fertilizers has stunningly shown great results in experiments. For more than a century, fertilizers have helped to sustain global agriculture, thereby contributing to global population and wealth growth [7]. Not only that, fertilizers contributions to crops have spared millions of hectares of natural ecosystems that otherwise would have been converted for agriculture [8].

Zeolite LTA (Linde Type A), also known as zeolite A, which belongs to the family of aluminosilicate molecular sieves [9], [10], is used as the soil nutrient retention to avoid leaking of fertilizer. It is characterized by the formula $|Na_{12}(H_2O)27|$ $8[Al_{12}$ Si_{12} $O_{48}]$ 8 which corresponds to its most common hydrated sodium form [11]. Zeolites has a three-dimensional (3-D) crystal lattice with loosely bound cations, which provides the capability of hydrating and dehydrating without altering the crystal structure [12], [13]. Moreover, the principal building units of zeolite A are sodalite cages, which form a 3-D network by connecting four-membered rings [13]. Its mesoporous structure that is able to trap ionic and molecular matters along with its capability for ion exchange has made this material widely used as a fertilizer additive. Furthermore, the advantages of zeolite as a slow-release fertilizer are that it is formed naturally as a non-toxic material, which is safe for humans, prevents nutrient leaching in soil, and is easy to apply to soil to remain fertilized for the entire growth season.

In this present work, zeolite LTA (Linde Type A) that is synthesized locally from Malaysian minerals is used as a soil nutrient retention agent to avoid leaking of fertilizer. Simple measurement techniques are introduced in the hope that people and society will be more interested in doing observation and investigation in agriculture field, which will undoubtedly have a significant impact on a county’s healthy social life and economy.

2. Material and Method

2.1 Materials

The raw kaolin obtained from Malaysia’s kaolin industry was used in the study. The sodium hydroxide used was from HmBG chemical with an analytical grade. The NPK fertilizer and mung bean seed is manufactured by New Trio Products.

2.2 Route to Synthesis Zeolite from Kaolin

The synthesis of zeolite involves two main processes, which are the thermal treatment of kaolin clay (calcination) to produce metakaolin and the hydrothermal synthesis of metakaolin to produce zeolite. The kaolin clay was sieved through a 63 µm sieve to obtain a finer powder. The kaolin clay was placed in a crucible and then heated in the furnace at 650 °C for 4 h. The calcination process that occurs when kaolin is heated has transformed it into metakaolin. Next, 3 g of metakaolin powder and 2M of sodium hydroxide (NaOH) were mixed with distilled water to make a 60 mL solution. The mixed solution was stirred at 40°C for 24 h by using a magnetic stirrer. The solution was then transferred into an autoclave and heated in the oven at 100 °C for 24 h. The hydrothermal synthesis, also known as crystallization, has transformed the metakaolin to zeolite. The heated solution undergoes a centrifugation process for 100 minutes. The water in the centrifuge tube was replaced every 10 minutes to reduce the pH level to neutral. The residue from the centrifugation process was left to dry in an oven at 60°C for 12 h to get the zeolite powder. The final product that was produced is zeolite powder.

2.3 Characterization of Kaolin, Metakaolin and Zeolite

The X-Ray Diffraction (XRD) Bruker D8 advanced machine was used in this study to investigate the crystalline phase of the kaolin clay and synthesized zeolite. The kaolin clay and synthesized zeolite were in powder form. XRD can determine all types of powder, fluids, and crystal materials’ crystalline phase and orientation. In addition, structural strain, phase composition, grain size, and thermal expansion can also be determined by using this machine. The scanning electron microscope (FESEM) was used in this study to determine the composition of each element of kaolin before and after going through hydrothermal synthesis. Not only that, the FESEM was used to determine the presence of NPK fertilizer coating on the zeolite. The FESEM is an incredible tool for observing the unseen worlds of micro-spaces. The FESEM shows very detailed 3-D images at higher magnifications than is possible with a light microscope. The images created without light waves are rendered black and white. Samples have to be prepared carefully to withstand the vacuum inside the microscope. Before the scanning process, the samples were sputter coated with a thin layer of gold using sputtering apparatus in order to make their surfaces more conductive and less susceptible to the accumulation of surface charge.

2.4 Growth Analysis

The growth analysis of the plant begins with weighing the NPK fertilizer and zeolite using a digital precision scale to obtain a precision of 0.3 g of fertilizer. The zeolite powder and fertilizer were mixed with 10ml of distilled water and stirred using a stirrer at 30 °C for 20 min. The solution of NPK fertilizer combined with zeolite powder was then poured onto the cotton wool and a seed was placed. The diagrams of the procedure are given as follows: Fig. 1(A) and Fig. 1(B). The physical characteristic of plant was observed including the leave length and stem height.

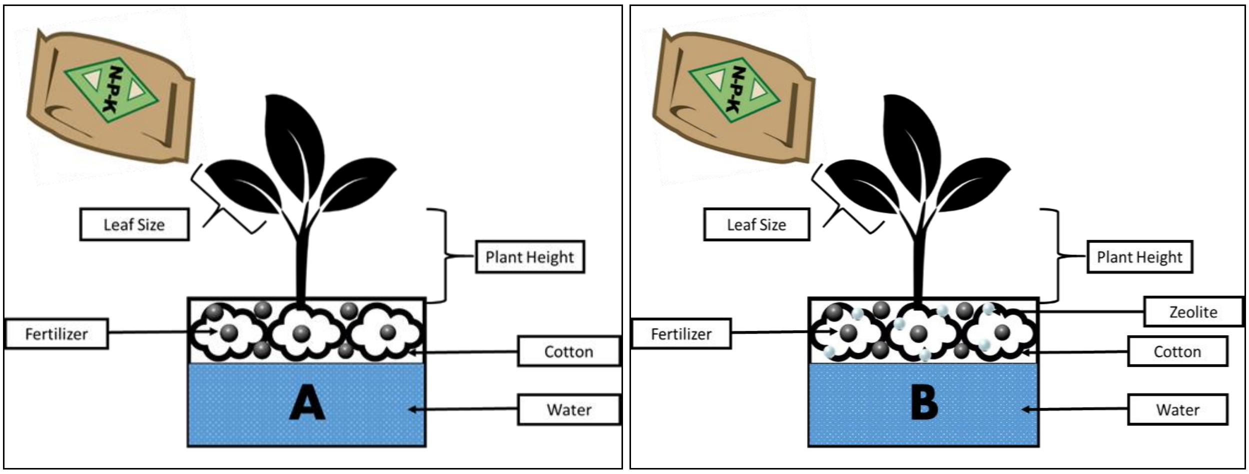


Fig. 1 - (a) Seed germination test without zeolite and; (b) seed germination test with zeolite

2.5 Adsorption Test

To study the adsorption performance of zeolite as a nutrient carrier with a pH variation ranging from 3-11 as shown in Fig. 2 and to determine the most suitable pH for crop growth and yields. For this experiment, five samples of mung bean seeds, each in separate containers, were placed in the same environmental conditions. For each of the samples, 0.3 g of zeolite was mixed with 0.3 g of NPK fertilizer in a solution of 150 ppm or 10 mL. The mixture is stirred using a magnetic stirrer each with variations of pH of 3,5,7,9, and 11 for 60 minutes. The mixture is then poured into each container containing the sample and is labelled with the respective pH values. The results of this experiment were tabulated and graphed to compare the adsorption performance of zeolite and crop growth and yield in a range of pH levels.

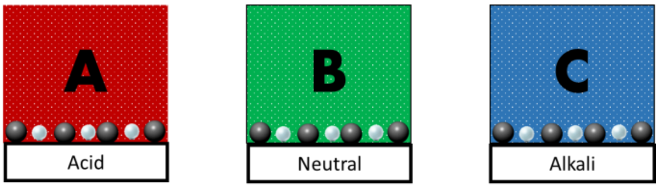


Fig. 2 - pH variation of NPK fertilizer based on zeolite

3. Results and Discussions

3.1 XRD analysis

The identification of the kaolin, metakaolin, and synthesized zeolite was performed by powder X-ray diffraction (XRD) on a Bruker D8 Advance with Ni-filtered Cu-K, radiation (1=0.154 18nrn), operating at 40 kV and 40 mA. Fig.3 (a), (b) and (c) show the differences in peak composition for kaolin, metakaolin, and zeolite LTA obtained from the XRD machine in which the pattern for Fig.3 (a) verified the existence of kaolinite and quartz in the raw kaolin with the composition of kaolin with 83.6 % kaolinite and quartz at 16.4 % [15]. Fig.3 (b) displays the analysis of data for the raw kaolin after being heat treated at 650 °C for 24 h. The data shows the presence of quartz as the main mineral and amorphous aluminio-silicate phase that was formed because of the reactions between SiO_2 and Al_2O_3 [15]. Fig.3 (b) depicts the composition of the quartz phase, which is entirely made up of metakaolin powder [16]. The following Fig.3 (c) shows the XRD analysis of synthesized zeolites. The pattern displays characteristics of highly crystalline material, showing sharp reflections of zeolite. The pattern of the sample displayed in Figure 1(c) shows the characteristic peaks that closely match with the findings of Tounsi, Mseddi, & Djemel [17] on the synthesization of zeolite LTA (Linde

Type A). The composition of zeolite LTA, which was 81.9 % and quartz, which was 18.1 % contained in the synthesized zeolite powder.

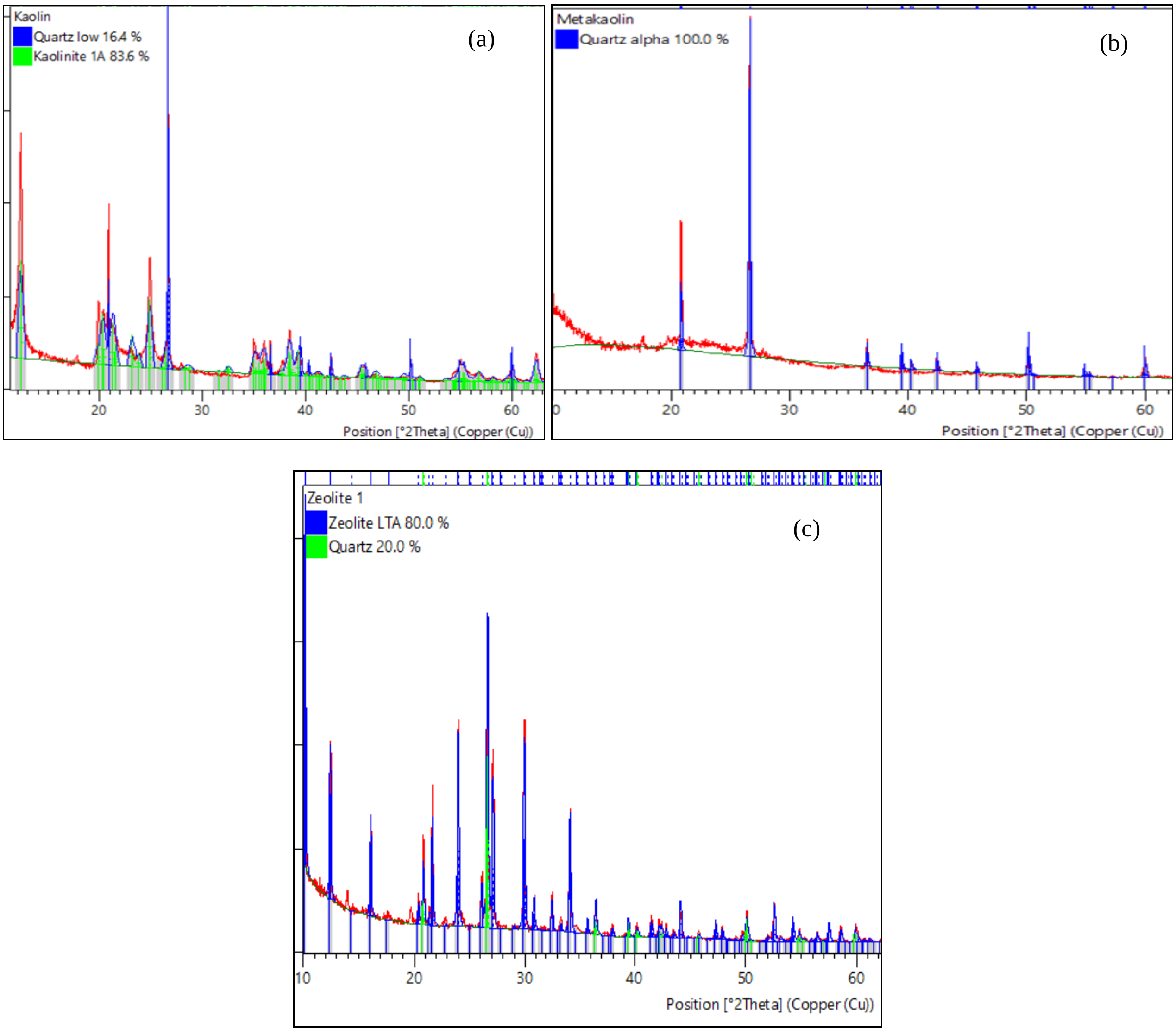


Fig. 3 - XRD for (a) kaolin; (b) metakaolin, and; (c) zeolite

3.2 Morphology Analysis

Measurement via FESEM is used to observe the morphology of powder as shown in Fig.4. This was to see the different sizes of particles and qualitative information regarding the morphology of powder. The raw material kaolin was seen to consist of small particles and flaky morphology structure at a magnification of 20k as shown in Fig.4 (a), which was similar to a study done by Khan [19]. However, upon the conversion to metakaolin, the flaky structure of kaolin has been altered, as shown at a magnification of 20k in Fig.4 (b). Meanwhile, Fig.4 (c) shows the formation of crystal and cubical with a sharp edge at a magnification of 5k, which confirms by the XRD analysis that suggested the formation of zeolite A with LTA structure. The result also was similar to a study conducted by Nyankson [19].

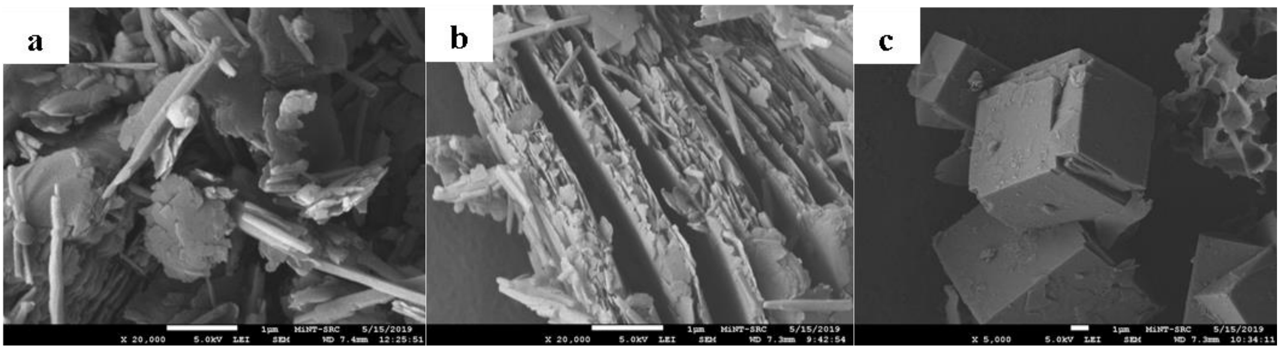


Fig. 4 - Fesem image of (a) kaolin; (b) metakaolin; (c) zeolite LTA

3.3 The Effect of the Presence of Zeolite On the Plant Growth

Table 1 shows the germination rate of mung bean seeds, where one plant has NPK fertilizer mixed with an adsorbent and the other without an adsorbent. Based on the 10 days of data collected, the germination rate of mung bean seeds with zeolite mixed NPK fertilizer was much faster compared to the mung bean with standard NPK fertilizer. It could be seen clearly that, the growth of stem and leaves for the plant with zeolite as an adsorbent was much faster compared to the plant without zeolite. Moreover, the rate of growth of plants without zeolite adsorbent reduced dramatically. This was due to the irrigation, which caused the plant to lose its important nutrients through leaching. However, the zeolite adsorbent plant showed a good rate of growth; the leaves looked much fresher compared to the plant without the zeolite adsorbent. This was due to the ability of zeolite to adsorb the nutrients released by the NPK fertilizer during irrigation. As a result, important nutrients are prevented from leaching into the soil or water.

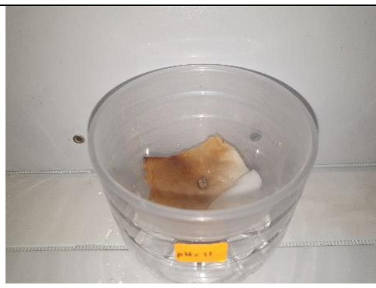
Table 1 - The germination rate of Mung Bean seed

Plant Type	Adsorbent	Time (day)	Average stem height (cm)	Average leaf length (cm)	Plant appearance (final day)
Mung Bean	None	1	0	0	
		2	0	0	
		3	0	0	
		4	0	0	
		5	0.21	0	
		6	0.37	0	
		7	1.82	0	
		8	3.34	0.92	
		9	6.87	1.34	
		10	8.73	1.87	
Mung Bean	Zeolite	1	0	0	
		2	0	0	
		3	0	0	
		4	0	0	
		5	0.47	0	
		6	0.51	0	
		7	1.30	0	
		8	4.00	1.27	
		9	8.20	2.25	
		10	12.50	3.20	

3.4 Effect On the Zeolite Absorption at Various pH-Soil On the Plant Growth

Table 2 represent the data on the effect of various pH on zeolite absorbability based on Mung Bean growth. The sample of plants grown in the environment with an initial pH reading of 5 and 7 show good crop growth and yield. However, it can be clearly seen that the crops grown below pH 5 suffer from the ability to germinate. This was due to the high intensity of acid that can be toxic to plants and was able to injure plant roots at pH readings below 5 [21]. Moreover, a study conducted by Onwuka [21] stated that plants' nutrients leach out of soils with a pH reading of below 5 more rapidly as compared to soils with values of 5.0-7.5. Not only that, the crops grown at a pH reading of 9 and above also suffer from seed germination. This proved the study conducted by Leonard [22], which states that the salinity and alkalinity that occurs at a pH reading above 8 where sodium and other salts are present at levels high enough to be harmful to plants. Based on Table 2, the crop grown at an initial pH level of 7 shows faster growth as compared to the crop grown at pH 5. This was due to zeolites' high adsorption of zeolite performance in pH reading of 7 as compared to pH reading 5 in adsorbing NPK fertilizer. A graph of summarize on the effect of various pH based on stem height and leaf length vs time is shown in Fig.5.

Table 2 - Effect of various pH on zeolite absorbability based on Mung Bean growth

pH	Time (day)	Average stem height (cm)	Average leaf length (cm)	Plant appearance (final day)
3	1	0	0	
	2	0	0	
	3	0	0	
	4	0	0	
	5	0	0	
	6	0	0	
	7	0	0	
	8	0	0	
	9	0	0	
	10	0	0	
5	1	0	0	
	2	0	0	
	3	0	0	
	4	0	0	
	5	0.32	0	
	6	0.65	0	
	7	1.10	0	
	8	3.28	1.20	
	9	7.50	2.38	
	10	9.10	3.00	
7	1	0	0	
	2	0	0	
	3	0	0	
	4	0	0	
	5	0.35	0	
	6	0.72	0	
	7	1.50	0.40	
	8	4.30	1.30	
	9	7.90	2.45	
	10	12.00	3.20	
9	1	0	0	
	2	0	0	
	3	0	0	
	4	0	0	
	5	0	0	
	6	0	0	
	7	0	0	
	8	0	0	
	9	0	0	
	10	0	0	
11	1	0	0	
	2	0	0	
	3	0	0	
	4	0	0	
	5	0	0	
	6	0	0	
	7	0	0	
	8	0	0	
	9	0	0	
	10	0	0	

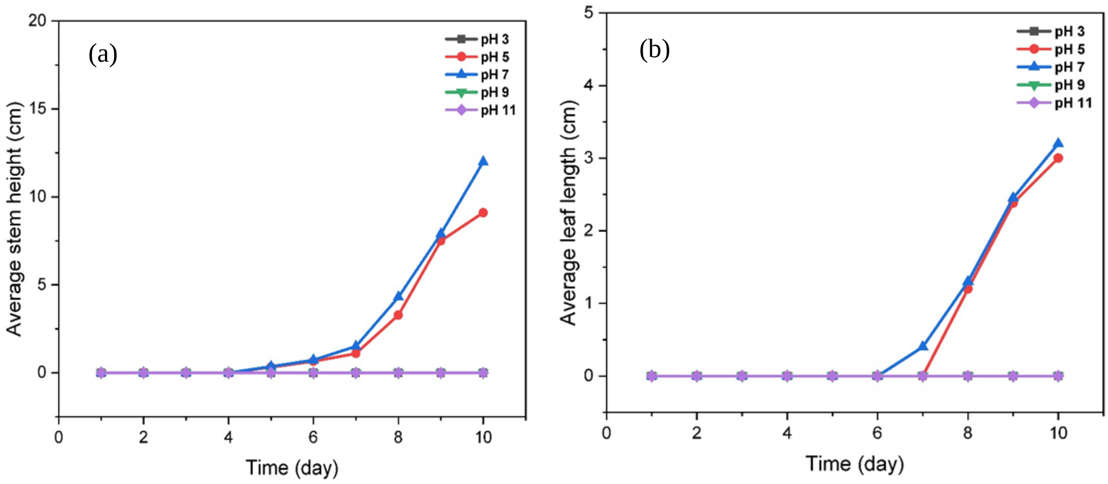


Fig. 5 - Graph of Mung Bean (a) average stem height vs time, and; (b) average leaf length vs time

4. Conclusion

The zeolite LTA was successfully synthesized from low grade kaolin using a simple hydrothermal technique. Further observation also revealed that this synthesized zeolite is able to absorb and sustain the nutrients from fertilizer to support the plant's growth. The Mung Bean (*Vigna Radiata*) growth ingrate with zeolite showed a better condition of plant growth as compared to mung bean without zeolite. Compared to normal NPK fertilizer, NPK fertilizer integrated with zeolite provided sufficient nutrients, which had a significant effect on promoting high yield and crop growth. Since the soil-pH plays an important role in plant growth, further observations were conducted to investigate the effect of soil-pH on zeolite performance as an absorbance. The zeolite at soil-pH 7 displayed a faster growth rate for mung bean plants for stem height and leaf length as compared to soil-PH at lower 7 and higher 7. This study demonstrated that zeolite synthesized from kaolin is able to provide multiple benefits in agriculture by acting as a nutrient carrier to avoid leaching of NPK fertilizer.

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