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RESEARCH NOTE

Characterization and Utilization of Zeolite for NPK Slow Release Fertilizer

T. E. Agustina*[a], I. Rizky[a], M. E. W. Utama[a], M. I. Amal[b]

[a] Chemical Engineering Department, Universitas Sriwijaya, Palembang, Indonesia
[b] Material and Metallurgy Research Center, Indonesian Research Institute, Serpong, Indonesia

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ABSTRACT

Based on various characteristics of zeolite, its utilization in the manufacture of fertilizers with slow-release properties is possible. The objectives of this study are to characterize and utilized nitrogen, phosphorus and potassium (NPK) slow release fertilizer by using natural zeolite in Indonesia. In this research, zeolite was utilized as a mixture of Slow Release Fertilizer (SRF). Effect of zeolite addition to single/multi-nutrients NPK fertilizer, compacting process, and applied medium on the average rate of fertilizer solubility was investigated. Fertilizer compaction results of NPK, NPK + zeolite, and (N-P-K) + zeolite were characterized by SEM EDS to examine the surface morphology and chemical composition of the fertilizer samples. Nutrients content in soil, domestic water, and demineralized water medium were analyzed by AAS. Base on the experimental results, it was found that addition of zeolite in the single (N-P-K) or multi-nutrients (NPK) fertilizer reduced the average rate of solubility of nutrients in the leaching medium. The results of this study showed that (N-P-K) + zeolite fertilizer has the lowest average rate of solubility than the other samples, it was proved by its average rate of solubility in soil, domestic water, and demineralized water medium, i.e. 9.63 ppm/h, 23.97 ppm/h, and 14.68 ppm/h, respectively.

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1. INTRODUCTION

A fertilizer is any material of natural or synthetic origin that is applied to soils or to plant tissues to supply one or more plant nutrients essential to the growth of plants. Fertilizer is used as the growth and development supporting medium for plant life. Nutrients contained in the fertilizer can make plants grow better compared to the nutrients contained in the soil. Availability of fertilizers is now rapidly expanding. Several types, shapes, colours, and brands of fertilizers are available. Fertilizer procurement deficiencies can lead to lower harvest production. Therefore, the availability of fertilizers should be balanced and stable. Inefficient fertilizer production, limited supply of raw material for fertilizer, and the rise of fertilizer prices are fertilizer smajor problem in Indonesia. Based on these issues, a better production technology is needed. Fertilizers are classified in many ways. They are classified according to whether they provide a single nutrient. Multi-nutrients fertilizers are most common. NPK fertilizers are three component fertilizers providing nitrogen, phosphorus, and potassium. On the basis of the needs of plants, manufacture of NPK fertilizers can be formulated with a single fertilizer such as urea fertilizer (containing dominant element of N), phosphate fertilizer/SP-36 (containing dominant element of P), and KCl (containing element of K). An equivalent content of NPK fertilizer can be replaced by combination of such single fertilizers. Zeolites are the most important family in microporous materials. Its characteristics are very stable with a very high adsorption capacity, selective, and also has many active pore structure which can hold water or nutrients. There are widely use of adsorbent which reveal high adsorption and separation capacities [1]. Having the properties of high specific surface area and cation exchange capacity (CEC), makes the zeolite has the potential to be further processed into broad application

*Corresponding Author's Email: tuty_agustina@unsri.ac.id (T. E. Agustina)

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products such as catalyst, catalyst-supporting, slow release substances, and membrane that have a high economic value. Highly diverse applications of zeolite make it a popular material for research and observation. Its application in separation process such as in petrochemical industry and enviromental area have been reported [2-5]. According to the various advantageous characteristics of the zeolite, its utilization in the manufacture of fertilizers with slow release properties is very prospective. Slow release fertilizer (SRF), which is a type of fertilizer that is capable of controlling the speed of release of nutrient elements that easily loose due to dissolvation in water, evaporates and denitrification processes of fertilizer itself. So the nutrients are available gradually over time. This is how most plants prefer to be fed and made them grow well. SRF will give many benefits for environment because the plants can absorb nutrients optimally so the nutrients release to the environment can be minimized. There are several advantages of SRF compared with conventional chemical fertilizers. First, SRF can reduce the inefficient utilization of fertilizers used by farmers. Second, the application of SRF can be performed only once in a growing season. Compared to prilled urea given 2-3 times, then the SRF fertilizer can save labour costs. Third, the use of zeolites in SRF formula can help improve soil fertility, because the zeolite has a quite high cation exchange capacity (CEC). Land that has a high CEC is one indicator of fertile soil. Fourth, the SRF is an environmentally friendly fertilizer. SRF is made from ingredients of formulated chemical fertilizers with metrics of natural zeolite in the form of granules with a size of 3-5 mm by using a binder that is easily decomposed by microorganisms (biodegradable). The SRF fertilizer will not have a negative impact on the environment because all the ingredients are chosen from nature.

However, addition of zeolite on NPK fertilizer will adsorb the NH_4^+, K^+, and $H_2PO_4^-$ ions released by fertilizer. If the required ion concentration in the soil decreases, $NH4^+$, K^+, and $H_2PO_4^-$ ions adsorbed by the zeolite will be released back into the soil solution, in this way the elements of N, P, and K which are given into the soil can be available in a longer time. Fertilizer in the form of SRF can optimize the absorption of nutrients by plants and maintain the presence of nutrients in the soil, because the SRF can control the release of the elements in accordance with the time and the needs of crops. Moreover, the size of fertilizers is very influential on the preferences of farmers. However, the farmers prefer to use granular fertilizer by spread system. Therefore, the SRF is manufactured by following the preferences of the farmers. The application of SRF make agricultural production more efficiently. The SRF is the best fertilizer chosen for vegetables, the nutrients will be maintained even in a particular season [6].

In this study, the slow release fertilizer was made by mixing single/multi-nutrients fertilizer and zeolite through the milling process. The method of ball milling is a widely used process in which mechanical force is used to achieve chemical processing and transformations. It is possible to synthesize chemical products using only mechanical action by a process known as mechanochemical. SRF have been created through this method such as synthesis of $KMgPO_4$ and $NH4MgPO_4$, kaoline–KH_2PO_4 and kaoline–$NH_4H_2PO_4$, and K-Si-Ca-O compounds [7-10]. Different material and compound have been also developed as the fertilizer mixed to enhance the ability of SRF to hold the nutrient released, such as kaoline, silica, and alumina [8-10]. In the current research, zeolite which have an adsorbent characteristic was utilized as a mixture of SRF.

Based on the mechanism of adsorption, the adsorbate molecules with a diameter equal or smaller than the diameter of the cavity pore can be adsorbed, whereas molecules with diameters larger than the pores of the adsorbent will be retained. In this case the diameter of the ion content in the fertilizer is smaller than the pore of zeolite so that the fertilizer ions can be absorbed into the zeolite.

The less fertile soils require a higher dose of fertilizer, because the content of $NH4^+$, K^+, and $H_2PO_4^-$ ions in the prilled of NPK and NPK tablet, could not adsorbed by soil particles, so there will be a high concentration of ions in the soil solution at the initial stage of fertilizer application, causing a greater loss percentage of fertilizer. However, there is an exchange mechanisms in the crystal lattice of zeolite in NPK-zeolite tablets. The NPK-zeolite fertilizer applied would be more efficient to use by the plant because the $NH4^+$, K^+, and $H_2PO_4^-$ ions firstly adsorbed by zeolite crystals before used which causes a higher efficiency application.

The objectives of this study are to characterize and utilize NPK slow release fertilizer using natural zeolite in Indonesia. Effect of zeolite addition to single/multi-nutrients NPK fertilizer, compacting process, and applied medium on average rate of fertilizer solubility was determined.

2. MATERIALS AND METHOD

2. 1. Materials Preparation Urea fertilizer (46% N), SP36 fertilizer (36% P), and KCl fertilizer (45% K) were used as the single nutrient fertilizer (N-P-K). Commercial NPK (16:16:16) fertilizer was used as multi-nutrients fertilizer. Natural zeolite was found from West Java. All sample sizes were reduced by mechanical milling. Certain amount of sample was formulated and homogenized. The sample mass comparison is shown in Table 1.

2. 2. Compacting Process The formulated samples were homogenized and further weighed 10 g. A press machine was used for compacting process using hydraulic pressure of 27,000 kPa. The process was run for 3 minutes. Once the process was completed, the solid pieces of sample were formed.

2. 3. Characterization and Analysis Method Total Dissolved Solid (TDS) measurement was used to determined the amount of dissolve solid from fertilizer sample in testing medium. Soil, domestic water, and demineralized water were used as the testing medium. TDS measurement was done in every 24 h using a TDS Meter. Fertilizer compaction results of NPK, NPK + zeolite, and (N-P-K) + zeolite were characterized by Scanning Electron Microscope Energy Dispersive Spectroscopy (SEM EDS). A JEOL JED-2300 JAPAN was used to examine the surface morphology and chemical composition of the fertilizer samples. Prior to use, a zeolite analysis was performed using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) to determine the composition of content and the purity of sample. A Rigaku SmartLab 3 kW XRD and TORONTECH TT-EDXPRT XRF were used in this study. Nutrients composition in soil, domestic water, and demineralized water medium were analysed by Varian Z88 of Atomic Absorption Spectrophotometry (AAS).

2. 4. Experimental Procedure Research procedure consist of preparation of fertilizer and natural zeolite. Mechanical milling was applied for mixing process and size reduction of certain formulated material. After milling, the powder material was compacted to get pellet material. Then leaching test was applied by using soil, domestic water, and demineralized water medium. The pellets material were put in the medium and add a certain volume of water regularly. In every 24 h samples were taken for TDS and AAS analysis.

3. RESULTS AND DISCUSSION

Materials that come from nature tend to have more secondary phases than materials derived from synthetic processes. Natural zeolites contain major compounds such as SiO_2, Al_2O_3, as well as supporting compounds such as K_2O, Fe_2O_3, CaO, MgO, and P_2O_5. The XRF analysis results are summarized in Table 2.

The XRD pattern of natural zeolite used in this study is in accordance with the mordenite and SiO_2 patterns listed in the International Center for Diffraction Data (ICDD) database with the database number of 00-029-1257 for mordenite and 00-083-0539 for SiO_2. The diffraction pattern is shown in Figure 1. The mordenite pattern is indicated by the black line while the SiO_2 compound which has the highest percentage is indicated by red color. Separate mordenite and SiO_2 peaks occur because of the secondary bonds between Al and Si are in pairs, the number of Si is greater than the number of Al so that the Si experiences free bond and forms a different new peak from the mordenite phase. From this result it can be concluded that the Si/Al ratio in this zeolite is stable, can be seen from the dominant peaks and supported by the data generated on the XRF test with the Si/Al ratio of 5.43.

Furthermore, the NPK fertilizer made from single nutrients (N-P-K) has lower average rate of solubility than NPK multi-nutrients fertilizer, as shown in the figure. In this research, the effect of compacting process on average rate of solubility was carried out by leaching of two different samples of NPK multi-nutrients fertilizer. It was found that the average rate of solubility of compacting NPK fertilizer is lower than non-compacting NPK fertilizer (granules).

The compacting NPK fertilizer has a smaller surface area than non-compacting NPK fertilizer. The compacting process of fertilizer actually does not effect significantly on the average rate of solubility but it makes the average rate of solubility of fertilizer a little bit slower. Effect of compacting process on average rate of solubility in domestic water medium was illustrated in Figure 2 (b).

Effect of leaching medium on average rate of solubility of fertilizer was studied. Soil, domestic water, and demineralized water were used as leaching medium.

TABLE 1. Sample mass comparison of formulated Slow Release Fertilizer

Sample	Sample mass (g)						Total (g)
	NPK	Zeolite	Urea	SP36	KCl	Milling Ball	
NPK	166.7	-	-	-	-	333.3	500
NPK + Zeolite	55.6	111.1	-	-	-	333.3	500
(N-P-K) + Zeolite	-	111.1	19.3	24.7	19.7	333.3	500

TABLE 2. XRF analysis result

No.	Compound	%
1.	SiO_2	69.75
2.	Al_2O_3	12.84
3.	K_2O	5.17
4.	Fe_2O_3	4.36
5.	CaO	4.06
6.	MgO	1.71
7.	P_2O_5	0.55

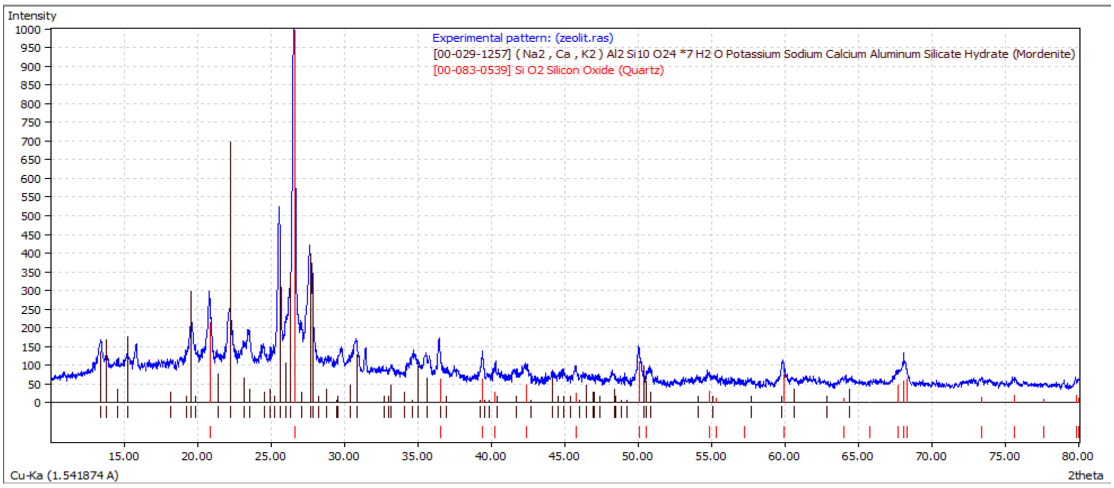


Figure 1. Diffraction pattern of natural zeolite powder (100 mesh)

Based on obtained results in soil medium, the average rate of solubility of non-compacting NPK, compacting NPK, NPK + zeolite, and (N-P-K) + zeolite were 81.03 ppm/h, 66.97 ppm/h, 56.37 ppm/h, and 9.63 ppm/h, respectively.

The average rate of solubility of non-compacting NPK fertilizer was the highest, as demonstrated in Figure 2. It is proved that the non-compacting NPK fertilizer (granules) was more soluble than the others fertilizer.

In domestic water medium, the average rate of solubility of non-compacting NPK, compacting NPK, NPK + Zeolite, and (N-P-K) + Zeolite were 75.77 ppm/h, 74.77 ppm/h, 56.37 ppm/h, and 23.97 ppm/h, respectively. However, in demineralized water medium, the average rate of solubility of non-compacting NPK, compacting NPK, NPK + Zeolite, and (N-P-K) + Zeolite average rate of solubility of non-compacting NPK fertilizer was the highest, though the value was not much different compare to compacting NPK fertilizer. However, the (N-P-K) + zeolite fertilizer has the lowest average rate of solubility in soil, domestic water, and demineralized water are shown in Figures 2(a), 2(b), and 2(c).

The structure of the surface morphology of the sample can be seen from the SEM characterization in Figures 3(a), 3(b), and 3(c). These Figures respectively show the microstructure of NPK, NPK + zeolite, and (N-P-K) + zeolite samples after milling and compacting process. All the three sample particles in sub-micron size can be synthesized by the milling process. NPK fertilizer which is milled and compacted shows a clot structure.

This is because the fertilizer is hygroscopic, causing the samples are agglomerated, as shown in Figure 3(a). Meanwhile, NPK fertilizer which is milled together with zeolite looks blended between the samples of fertilizers and zeolite but still lumpy, as demonstrated in Figure 3(b).

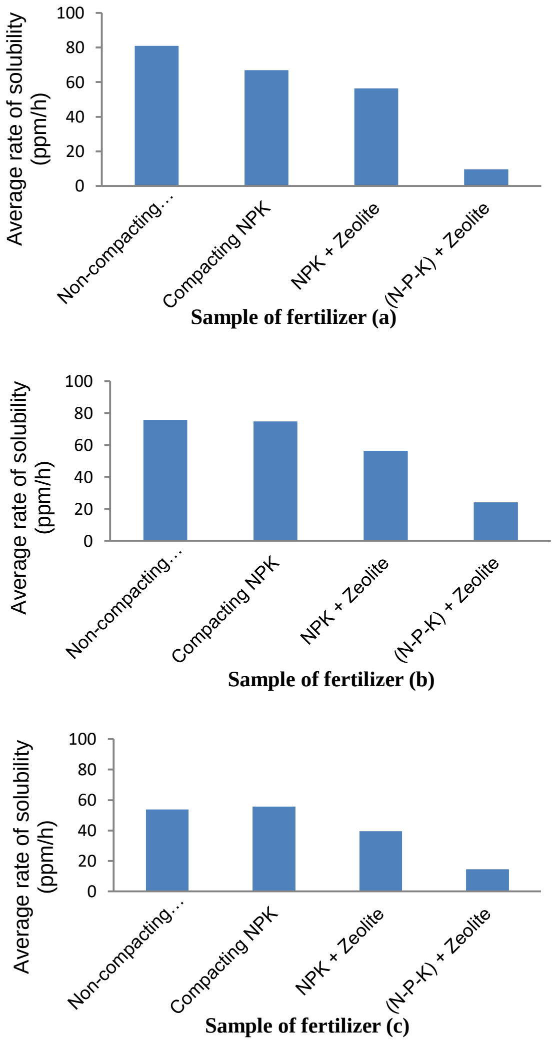
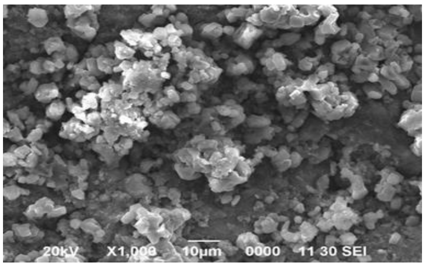
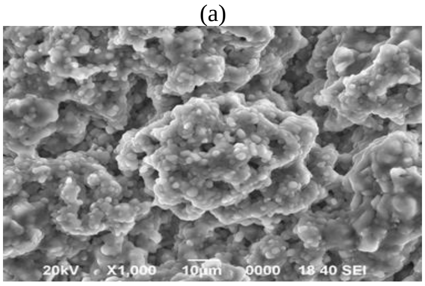


Figure 2. Average rate of solubility of fertilizer in (a) soil medium, (b) domestic water medium, (c) demineralized water medium



(a)



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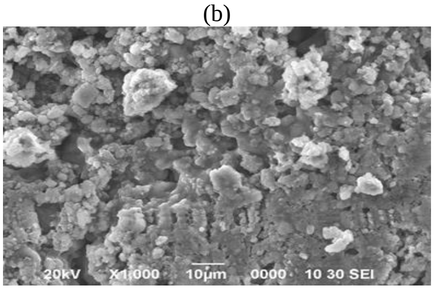

(c)

Figure 3. SEM images of (a) NPK fertilizer, (b) NPK + Zeolite, (c) (N-P-K) + Zeolite

However, (N-P-K) fertilizer milled together with zeolite shows the improvement of blending compared to the previous samples, as presented in Figure 3 (c).

The last samples do not agglomerate and form a solid flat that make these samples have a better slow release properties. To produce a more homogenous size and fine, the milling process can be extended. The results of the microstructural observations also indicate that the samples have relatively good density or are sufficiently compact so that the sample strength is also higher than the granular shaped samples which is not given the treatment.

EDS results show components such as P, K, Mg, Si, and O. However, some components such as N are not detected properly because N is still in the form of organic compounds, while EDS is more sensitive to the analysis of elements. The EDS analysis results are summarized in Table 3. The (N-P-K) + zeolite fertilizer has the highest Si percentage that affects the ability to adsorb. The results of AAS analysis in demineralized water were depicted in Figures 4 and 5. It can be seen in Figure 4 that within 168 hours the total elements of N, P, K in the fertilizer were 100% released in the demineralized water.

However, until 288 hours the release percentage of N, P, and K elements were 85, 80, and 75%, respectively (see Figure 5). Based on these figures, the addition of zeolite as a mixture of NPK slow release fertilizer can withstand the release of nutrients in the fertilizer.

TABLE 3. SEM EDS analysis result

No	Sample	Elements composition (%)										Total (%)
		N	O	Mg	Al	Si	P	K	Ca	Fe	Cl	
1	NPK	-	46.55	1.30	2.07	6.24	-	1.28	40.43	2.12	-	100
2	NPK + Zeolite	-	10.19	0.27	-	0.34	5.07	4.95	78.74	-	0.44	100
3	(N-P-K) + Zeolite	-	49.20	-	2.93	12	0.77	29.95	-	-	5.14	100

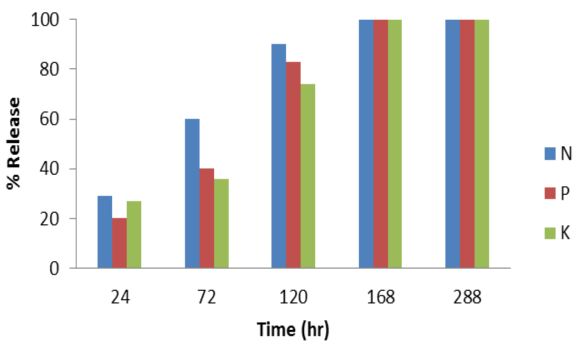

Figure 4. Release percentage of nutrients in NPK fertilizer (granules) during leaching test

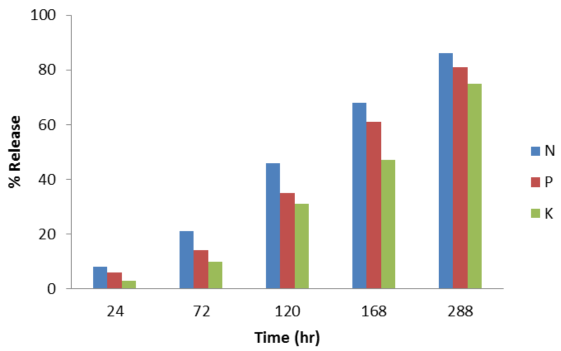

Figure 5. Release percentage of nutrients in NPK + zeolite fertilizer during leaching test

4. CONCLUSION

Addition of zeolite in single (N-P-K) or multi-nutrients (NPK) fertilizer reduced the average rate of solubility of nutrients in the leaching medium. Furthermore, the compacting process of fertilizer did not effect significantly on the average rate of solubility but it makes the average rate solubility of nutrients a little bit slower. The results of this study showed that (N-P-K) + zeolite fertilizer had the lowest average rate of solubility than the other samples. It was proved that its average rate of solubility in soil, domestic water, and demineralized water medium were 9.63 ppm/h, 23.97 ppm/h, and 14.68 ppm/h, respectively.

5. ACKNOWLEDGEMENT

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Characterization and Utilization of Zeolite for NPK Slow Release Fertilizer

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T. E. Agustina[a], I. Rizky[a], M. E. W. Utama[a], M. I. Amal[b]

[a] Chemical Engineering Department, Universitas Sriwijaya, Palembang, Indonesia
[b] Material and Metallurgy Research Center, Indonesian Research Institute, Serpong, Indonesia

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چکیده

بر اساس ویژگیهای متنوع زئولیت، استفاده از آن در تولید کودهایی با خواص رهایش آهسته امکانپذیر است. اهداف این مطالعه توصیف و تولید کود با رهایش آهسته NPK با استفاده از زئولیت طبیعی در اندونزی است. در این تحقیق، زئولیت بعنوان مخلوطی از کود با رهایش آهسته (SRF) مورد استفاده قرار گرفت. اثر افزودن زئولیت بر کود NPK تک یا چند عنصری، فرایند تراکم و محیط کشت بر میانگین میزان حلالیت کود مورد بررسی قرار گرفت. نتایج تراکم کود برای NPK، زئولیت + NPKو زئولیت + (N-P-K) توسط SEM EDS مشخص شد تا ریخت شناسی سطح و ترکیب شیمیایی نمونه های کود مورد بررسی قرار گیرد. محتوای مواد مغذی درخاک، آب شهری و محیط آب کانی زدایی شده بوسیله AAS آنالیز شد. بر اساس نتایج تجربی، مشخص شد که افزودن زئولیت در کود تک عنصری (N-P-K) یا چند عنصری (NPK) میزان متوسط حلالیت مواد مغذی را در محیط اشباع کاهش داد. نتایج این مطالعه نشان داد که کود زئولیت + (N-P-K) کمترین میزان متوسط حلالیت را نسبت به نمونه های دیگر دارد که با میزان متوسط حلالیت آن در خاک، آب شهری، محیط آب کانی زدایی شده یعنی بترتیب 9/63 ppm/h ، 23/97 ppm/h، 14/68 ppm/h ثابت شده است.

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