

Full Length Research Paper

Effectiveness of urea nanofertilizer based aminopropyltrimethoxysilane (APTMS)-zeolite as slow release fertilizer system

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In this study, nanofertilizer effectiveness of urea/APTMS-modified zeolite as a slow release fertilizer nitrogen from urea was evaluated. The natural zeolite is activated by 1% of HF with a temperature of 120°C and a zeolite surface has been modified with aminopropyltrimethoxysilane (APTMS) 5%. Zeolite was activated with APTMS-modified zeolite characterized by X-ray diffraction spectroscopy (XRD), surface area analyzer (SAA) and UV-Vis spectroscopy. Modification of activated zeolite with APTMS result in decrease in pore size as well as crystallinity. While the aminopropyl group was well defined with FTIR spectra, pore size measurement using SAA obtained APTMS-modified pore size was 7.74 nm; while a maximum adsorption capacity of urea was 3.668 mg/g. Slow release urea of APTMS-modified zeolite was evaluated and observed by the increasing of urea absorbance at a wavelength of 190 nm in aqueous media. The experiment result showed that urea without zeolite was released up to 100% limit at 10 min observations, while the urea impregnated with APTMS-modified zeolite in 1 M NaCl media was released up to 100% at 120 min observation times. Meanwhile, the APTMS-modified zeolite in aqueous media was released only about 56.24% at 120 min. The result conclude that the APTMS-modified zeolite is capable of retarding the release of urea and potential to be developed as a control release of nitrogen from urea.

Key words: Zeolite, modified aminopropyltrimethoxysilane (APTMS), urea, slow release fertilizer.

INTRODUCTION

Indonesia is the largest consumer of fertilizer, one of which is nitrogen fertilizer. In 2012, total demand reached 11.1 million tons of fertilizer. Therefore, fertilizer is a major issue for Indonesia. The high demand for nitrogen fertilizer is due to its having the most important element for crops such as rice, namely nitrogen (N). Despite the

relatively important element, nitrogen is an element with least efficient utilization as it is easily lost through leaching in the form of nitrate, evaporating into the air in the form of ammonia gas, and changed into other forms that cannot be utilized by the plant. One example of the type of fertilizer N often found in the market in Indonesia

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is in the form of urea ($\text{CO}(\text{NH}_2)_2$). Fertilizer is easily soluble in water and evaporates into the air so that nitrogen fertilizer is low fertilizer efficiency. When Nitrogen is applied into the soil, approximately 30 to 40% is taken by plants, and 60% is lost in the process of ammonia volatilization into the gas (De Datta, 1987).

Therefore, another innovation is required to improve the efficiency of fertilization. One attempt to reduce the nitrogen fertilizer by making it in a slow release form. Enterprises slow release of nitrogen fertilizer can reduce environmental pollution due to the release of nitrogen being controlled so that the amount of excess nitrogen in the form of nitrate that enters the water is reduced, thereby reducing water pollution. One of the materials that can be developed as a controller release nitrogen in fertilizer is a natural zeolite. Recently, several types of SRFs have been developed and tested, including SRFs using various zeolites. Bansiwali et al. (2006) was used to evaluate slow release phosphorous intake in surfactant modified zeolite (SMZ). The results indicated that SMZ is a good sorbent for PO_4^{3-} , and a slow release of P was achievable. Li (2003) has used surfactant-modified zeolite as fertilizer carriers to control nitrate release. However, SRFs are often expensive and the release of nutrients is slow at the time of high nutrient need (Miller and Gardiner 1998).

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, with a three-dimensional lattice, furrowed by an inner network of pores and channels. Zeolites have a high cation exchange capacity and have often been used as inexpensive cation exchangers for various applications (Breck, 1974; Barrer, 1976). The studies on SRFs based on zeolites are limited to nutrients, which can be loaded in cationic forms such as NH_4^+ and K^+ . However, if the nutrients are in anionic forms such as NO_3^- or PO_4^{3-} , the loading is negligible on unmodified zeolites.

Modification of natural zeolite with aminopropyltrimethoxysilane (APTMS) aims to increase the affinity uptake of urea in the framework of the zeolite pores, so it can control the release of urea nitrogen according to the time and amount needed. It can occur because the active amine groups on the APTMS will bind the nitrogen of urea compound so that the release of urea can be controlled. Using the APTMS-modified zeolites as urea intake medium, we have slow release fertilizer that is expected to optimize the uptake of nitrogen by plants and maintains the presence of nitrogen in the soil with the amount of fertilizers applied smaller than the conventional method.

Based on the description above, this research focuses on testing the efficiency of the modified natural zeolite nanoporous as a mixture of urea which is expected to help release of nitrogen from fertilizers. Preparation of slow release fertilizer (SRF) zeolite materials with the right amount is expected to control the release of nitrogen in accordance with the time and number of plants needed and maintain the presence of nitrogen in the soil, so that

a given amount of fertilizer is more efficient than conventional methods and can save costs.

METHODOLOGY

Natural zeolites activation

This is a method by Budi et al. (2013), in which natural zeolite is crushed and sieved to 60 mesh size to qualify. The zeolite was washed with distilled water and soaked in 1% HF for 10 min. Zeolite was thereafter washed with distilled water until neutral pH. Then, the zeolite was heated in an oven at 120°C for 4 h. After the acid activation procedure, the result was characterized using XRD (Bruker D8 Advance X-Ray Diffraction) to evaluate the diffractogram pattern of no activation and activated zeolite. Also, SAA (Surface Area Analyzer) measurement was used to determine the surface area of the activated zeolite.

Surface modification of activated zeolite

According to Zhao et al. (2012), activated zeolite was modified with silane agent of 5% APTMS, and then shaken for 8 h at room temperature with a speed of 150 rpm. It was thereafter washed with distilled water and dried. The APTMS-modified zeolite result was characterized by FTIR (Fourier Transform Infrared Spectroscopy) to determine the functional groups of aminopropyl attached to zeolite and SAA (Surface Area Analyzer) to determine the surface area of APTMS-modified zeolite.

Adsorption urea onto APTMS-modified zeolite

1.0 g of APTMS-modified zeolite was added to urea solution of 36.5 mg urea in 100 mL of distilled water. The mixture was mixed for 24 h at room temperature, and placed at a temperature of 40°C overnight. The obtained product was evaluated using FTIR (Fourier Transform Infrared Spectroscopy) to confirm the functional groups of urea attached to APTMS-modified zeolite.

Slow release fertilizer testing

Slow release fertilizer testing (SRF) was conducted with APTMS-modified zeolite, zeolite, urea and urea-APTMS without dissolving. 0.5 g of each sample was added to NaCl 1 M as well as to distilled water, and was then soaked at a speed of 140 rpm in room temperature. The solutions were measured using UV Vis spectrometer for each certain time (5 to 120 min) to calculate the urea released at λ_{max} 190 nm.

DISCUSSION

Urea is one example of fertilizer that has low absorption efficiency in soil which is in the range of 30 to 40%. Urea easily dissolves in water to form NH_4^+ cations. Therefore, one of the effort is how to improve the efficiency of urea fertilizer to temporarily bind into zeolite nanopore get the nanofertilizer approach. The first achievement of this research is activation of natural zeolite. The zeolite was destructed to about 60 mesh in size, to gain the homogenized size and enlarged surface area. Zeolite was activated through acidification using 1% HF solution

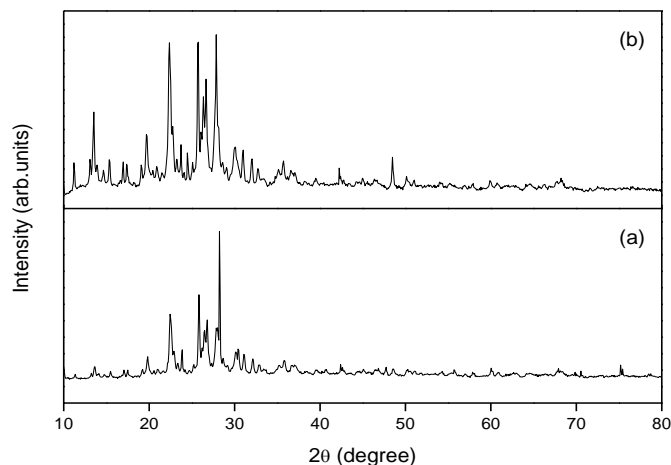


Figure 1. XRD pattern of (a) activated zeolite (b) natural zeolite used for SRF.

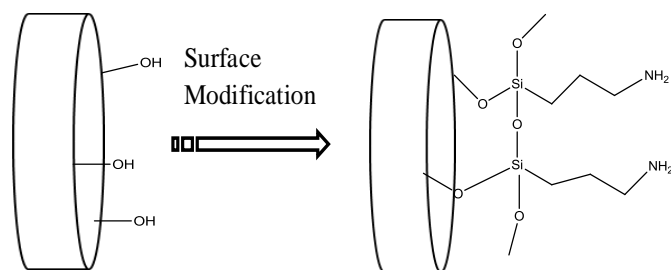


Figure 2. Mechanism of surface modification of zeolite by APTMS.

to dissolve the impurities of natural zeolite content. Acidified zeolite was then cleaned up until neutral condition was obtained and was thereafter dried at a temperature of 120°C.

In the acid activation process, silica dissolution process was adopted, which is one component of the zeolite framework (Jozefaciuk and Bowanko, 2002). Silica dissolution will lead to changes in the structure of the zeolite and the decreasing ratio of Si/Al. The decrease of Si/Al ratio may affect the zeolite adsorption capacity and selectivity towards polar molecules such as water vapor (Bonenfant et al., 2008). Figure 1 shows the XRD pattern of the zeolite before and after activation by 1% HF solution.

Results of the XRD analysis showed the presence of activated zeolite reduction of Si/Al ratio. It can be seen in the decrease in peak of SiO₂ and Al₂O₃ (Figure 1b). Decrease in the Si/Al ratio influence the zeolite pores due to a higher electric field impact increased "charge site" on the surface of the zeolite. In addition, decrease of Si/Al ratio also aims to remove certain ions from the zeolite framework.

Modification of activated zeolite using APTMS successfully influence the chemical properties of the

material. APTMS attach mechanisms into zeolite framework and can be assisted by zeolite surface activation in the previous stage. Aminopropyl group will attach to the pore zeolite surface to make monolayer formation. The purposed mechanism of surface modification of zeolite by APTMS was shown in Figure 2.

The FTIR analysis of the unmodified zeolite and APTMS-modified zeolite indicates that the modification process was successful. From the FTIR spectrum in Figure 3, it can be seen that there was a shift in the region of 1030 cm⁻¹ which was the absorption of the Si-O-(CH₂)₃NH₂. This shift may occur due to the molecular weights of compounds increases, so it will shift to the smaller wave numbers. In addition, the characteristic absorption of the primary amine from modified zeolites in the region 3000 to 3330 cm⁻¹ showed that the modification was successful. The intake of urea into APTMS-modified zeolite occur via chemical adsorption using aminopropyl group (Figure 3).

Urea is capable of interacting with aminopropyl to form linked amino. This have been observed by decrease in absorbance of UV Vis spectra which indicates the decrease of urea concentration in liquor medium. Based on the quantitative calculation from UV Vis spectroscopy data, the maximum adsorption capacity of urea by APTMS-modified zeolite was 3.668 mg/g, while the maximum adsorption capacity of unmodified zeolite reach only about 0.243 mg/g (Budi et al., 2013). It may be caused by differences in surface properties of zeolite and APTMS-modified zeolite. Adsorption on zeolites without modification occur as a result of the interaction of the charge and the zeolite pores properties, wherein the urea in solution will be trapped by the pores of the zeolite surface both external and internal. While in APTMS-modified zeolite, adsorption occurs by being trapped into pore zeolite via aminopropyl anchor as well as by electrostatic interactions on the surface of modified zeolite. The pore size and surface area measurements using SAA method were 7.74 nm in pore size and a surface area of 5.488 m²/g. The pore properties should influence adsorption capacity of urea.

SRF testing of urea in APTMS-modified zeolite in different media compared with untrapped urea were evaluated. The result of those analyses was shown in Figure 4. SRF evaluations were observed by the increasing of urea absorbance at a wavelength of 190 nm in aqueous media. Based on the experiment, it was observed that urea without zeolite was released up to 100% limit in 10th min observations, while the urea impregnated to APTMS-modified zeolite in 1 M NaCl media was released up to 100% at 120 min observation times. Meanwhile, the APTMS-modified zeolite in aqueous media was released for only about 56.24% at 120 min. It may be caused by ionic strength influence of salt content in aqueous medium. In the presence of NaCl solution, the system is more capable of making interaction than those without NaCl solution. The result concludes that the APTMS-modified zeolite is capable of

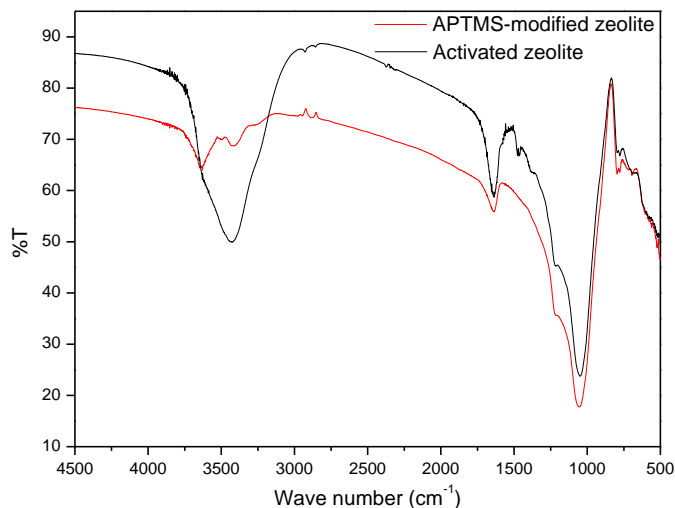


Figure 3. FTIR spectra between unmodified zeolite and APTMS-modified zeolite.

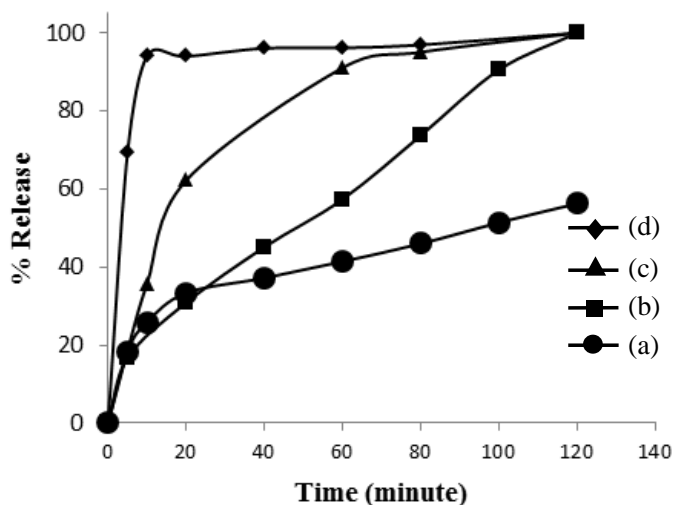


Figure 4. SRF test of urea with (a) APTMS-modified zeolite in aqueous media (b) APTMS-modified zeolite in 1M NaCl aqueous media (c) APTMS-modified zeolite without aqueous solvent (d) urea untrapped.

holding the release of urea and potentially to build a SRF system based urea fertilizer.

Conclusion

The study revealed that the SRF based urea system can be built by urea trapped in APTMS-modified zeolite. The APTMS-modified zeolite is capable of holding the release of urea by the chemical interaction between urea and APTMS-modified zeolite via amine linked. The ionic strength influence the capability of SRF. In the presence

of NaCl solution, the system is more capable of interaction than those without NaCl solution.

Conflict of Interest

The authors have not declared any conflict of interest.

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