Using of low grade zeolite based fly ash as slow release agent for Zea mays growth

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Abstract. The present work introduce synthesis low grade zeolite from fly ash and its application as urea slow release agent on Zea mays growth. The characterization of the synthesized zeolites were determined using X ray diffraction method and FT-IR spectroscopy. The zeolite that has been formed is added to urea fertilizer with a weight ratio of urea: zeolite as follows 1: 1, 1: 2, 1: 3. As much as 3 kg of soil is put in a polybag series and was added with 3 g urea slow release fertilizers. The polybags were planted with Zea mays plant 1 week in old at a depth of ± 5 cm. The plant growth parameters which include plant height plant, number and colour of leaves were observed every 7 days for 4 weeks. Base on the diffraction pattern and IR spectra, the characteristics of the synthesized zeolite is matching with standard zeolite A. The use of urea slow release fertilizer on Zea mays plants showed better growth than using urea fertilizer without zeolite slow release ingredients. The treatment of soil with urea/zeolite 1:3 proven to produce the best Zea mays growth in interaction time 4 weeks.

1. Introduction

Coal is a fossil fuel whose users are increasingly addicted as increasing the human needs in various fields, especially in the cement industry and coal-based power plants. The domestic needs of coal for requirements the electricity power plant in Indonesia were predicted reached 97 and 162 million tons respectively at 2018 and 2027 [1]. In global scale, World Energy Resources explained that coal will still play a key role as an energy raw material, and responsible for 40% of the world’s electric energy supply [2]. However, the use of coal in industry produce not only energy, but also solid waste in the form of fly ash and bottom ash which continues to increase. The amount of produced coal ash in the United States reached more a billion tons and much more in the worldwide [3]. In 2015, the global produced fly ash reached more than 1 billion tons [4].

Solid waste of coal fly ash has been an environmental problematic for many countries in the world. The fine particles of fly ash reach the pulmonary region of the lungs and remain there for long periods of time; they behave like cumulative poisons [5]. Government Regulation of Republic Indonesia No. 88 of 1999 explains that, fly ash waste can be categorized as toxic and dangerous material waste. The increasing need for coal as fuel, of course it will result in an increase of fly ash produced. This accumulation of fly ash if not utilized will cause the serious environmental pollution. Therefore, efforts are needed to utilize fly ash in various purposes. One of them is turning it into zeolite which can be used in various field. Coal fly ash is the major residue from coal combustion and comprised mainly of fine-grained particles of SiO2 and Al2O3 [6]. The oxides component of fly ash Suralaya Power Plant comprise SiO2, Al2O3, Fe2O3, CaO respectively 62.98; 26.73; 4.49 and 1.52% [7]. Using NaOH as mineralizer can converted fly ash to zeolite which can be utilized in agriculture [8].
In agriculture, the use of fertilizer containing nitrogen, phosphor and kalium tend to increase along with the increasing need for food. Urea, phosphate and nitrate fertilizers are easily soluble in water and easily carried by water when used in fertilizing of plants. Therefore the fertilizer absorption by plants is less effective and precisely can pollute the environment due to release nitrate and phosphate. In order to minimize the contamination caused by nitrate and phosphate compounds and to maximize the use of these fertilizers, can be used slow release fertilizer, SRF [9]. The fertilizers can control the release of nutrients in the soil during fertilizing. SRF is a fertilizer that has the characteristic of being able to release its nutrients slower than other conventional fertilizers. SRF is made from a mixture of fertilizer and agent slow release. Because of its nature as a porous material and ion exchange, zeolite is often used as a slow release agent. Modification of zeolites using nano composites is very environmentally friendly if used as a slow release fertilizer [10].

For the purpose of fertilizing the soil in support of the growth of various plants in general use urea fertilizer. Urea is produced by reacting ammonia and carbon dioxide. the first reaction is \( \text{CO}_2 + \text{NH}_3 \rightarrow \text{NH}_2 \text{CO}_2 \), then dehydrates into urea and water [11]. Urea fertilizer has water-soluble properties, so that when used in fertilization, urea is easily released back from the soil before it is absorbed by plants and dissolved by water. The excessive use of urea fertilizer is not only inefficient, but can also cause serious environmental pollution problems. Nitrate contamination in water is mainly caused by excessive use of fertilizers, increased agricultural activity and by human and animal waste. The increase in nitrate and phosphate content in waters can accelerate the growth of weeds and algae blooms. In addition, presence of nitrates in the water besides causing fertile weed growth can also cause methemoglobin in children and infants. High levels of nitrates in drinking water can cause methemoglobinemia, commonly called blue baby syndrome [12]. Methemoglobin is a condition where the blood is unable to bind oxygen [13]. Therefore, efforts are needed to minimize the nitrate and phosphate fertilizing impact. One of them is by using zeolite as a slow release fertilizer agent in the use of urea fertilizer. The use of zeolites in nitrogen compound fertilizers, delay and potassium can reduce the average solubility of nutrients in soil, domestic water, and demineralized water media [14].

Zeolites are characterized by their ability to absorb and remove water and exchange part of their cations without changing their crystal structure [15]. Synthesis of zeolites is generally carried out through a hydrothermal process [7, 16, 17]. In hydrothermal synthesis is mostly carried out at moderate temperatures and low vapor pressure. However, the nature of pure water solvents is often not enough to dissolve substances in the crystallization process, even at high temperatures, so a mineralizer needs to be added, commonly used for \( \text{SiO}_2 \) are \( \text{NaOH} \). In this study, we convert coal fly ash to low grade zeolite using hydrothermal method. The product of zeolite were applied as slow release agent for \( \text{Zea-mays} \) growth. The characteristics of product zeolite and the growth parameters of \( \text{Zea mays} \) were also studied.

2. Methods

2.1. Materials and equipment

The materials used in this study were fly ash, urea fertilizer and soil. The used chemical comprise sodium hydroxide, hydrochloric acid, analytical grade produced Merck, sodium aluminat analytical grade from Sigma Adrich. The equipment tools used in this study include a set of glassware, furnaces, reflux devices, stirrer bars, hydrothermal devices, Oven (Memmert), FTIR Perkin Elmer Spectrum 100, XRD BRUKER 6000, a set of electrical sieve, digital balance sheet (Ohaus Explorer), filter paper Whatman 42, universal indicators and polybag.

2.2. Preparation zeolite from coal fly ash

The transformation of fly ash into zeolite A is carried out through a series of synthesis process, based on a modified hydrothermal method developed by Jumaeri et al. [7]. The fly ash which will be used previously is sieved at 170 mesh. These fly ash samples were subsequently refluxed with 1 M HCl solution to increase their activity in zeolite formation. The refluxed fly ash was mixed with NaOH in a weight ratio of 1: 1.2. After going through the initial dissolution and paste and evaporation stages, this mixture is melted in a stainless steel crucible, at a temperature of 600°C for one hour. The resulting melting mixture is then cooled to room temperature. After hydrothermal synthesis, the product
obtained was then washed with distilled water to pH 10. Then filtered and dried at 60°C for 12 hours. Furthermore, the synthesized zeolite crystals were characterized qualitatively using Infrared Spectroscopy, Perkin Elmer FTIR, Shimadzu XRD-6000 X-ray Diffraction and Scanning Electron Microscope (SEM).

2.3. Preparation of slow release fertilizer (SRF)
Preparation SRF is based on the modified research of Sriatun et al. [18]. Zeolite that has been formed is added to urea fertilizer with a weight ratio of urea: zeolite as follows 1:1, 1:2, 1:3, and referred to as SRF-1, SRF-2 and SRF-3. Table 1 shows the composition of urea and zeolite for the manufacture of 1 kg SRF.

Table 1. Composition of SRF- urea

| SRF Code | Urea (g) | Zeolite (g) |
|----------|----------|-------------|
| SRF-1    | 500      | 500         |
| SRF-2    | 333      | 677         |
| SRF-3    | 250      | 750         |

2.4. Application SRF for Zea maize growth
The urea SRF application used is based on the modified Sriatun method [18]. As much as 3 kg of soil is put in a polybag series. Furthermore, each polybag was added with 3 g urea- SRF-1, SRF-2 and SRF-3 urea. The polybags were planted with Zea mays plant 1 week in old at a depth of ± 5 cm. The plant growth parameters which include plant height plant, number and colour of leaves were observed every 7 days for 4 weeks.

3. Result and discussion

3.1. Diffractogram of zeolite synthesis
The diffractogram of the Suralaya power plant fly ash and zeolite synthesized are presented respectively in Figure 1a and 1b. From the picture there is a very significant difference in diffraction patterns between fly ash (FA) and zeolite synthesized from FA (ZFA).

![Difractogram of: (a) FA and (b) ZFA](image)

The Suralaya power plant fly ash is composed of amorphous and crystalline phases of quartz, mullite and hematite. Meanwhile the synthesized zeolite diffractogram shows the new peaks are typical for zeolite and the component quartz, mullite and hematite is very low in intensity. This indicates that the fly ash has been converted to low grade zeolite. The diffraction peaks of fly ash have turned into typical zeolite A peaks. The ZFA diffractogram were showed at 2 theta: 10.42; 12.72; 14.20; 24.56;
26.38; 27.36; 31.42; 31.78 and 34.88° which matching with 2 theta zeolite A standard Wako at previous research [7]

3.2. Infrared Spectrum of synthetic zeolite
Infrared spectra provide structural information (functional groups) of the material being studied. The measurement results using Infrared Spectroscopy (IR) of coal fly ash and synthesized zeolite are listed in Figure 2.

![Figure 2. Infrared spectra of : (a ) FA and (b) ZFA](image)

The IR spectra in Figure 2 shows the presence of fly ash absorption bands at wave number 3425 cm^{-1}, which indicates the existence of O-H bond vibrations, while at 2366 cm^{-1} shows the presence of Si-H groups in fly ash. Zeolites obtained using NaOH show spectra similar to Zeolites A. The main absorption band is at wave number 3426; 1651; 1011; 556; and 463. Similar spectra were also obtained, namely the peak characteristic of the zeolite A Wako, at wave numbers 3448.72, 1651.07, 1002.98, 663.51, 555.50, and 462.92 cm^{-1} [7].

3.3. Application of SRF Urea on Zea mays growth
Growth of Zea mays plants can be determined by the parameters of plant height, number of leaves, and leaf color. The process of plant growth is certainly influenced by many factors including the environment, physiology and genetics of plants. The plant height is a plant size that often observed both as an indicator of growth and as a parameter used to measure environmental influences or the treatments applied [19]. The effect of using SRF on performance of the Zea mays growth using zeolites were synthesized from fly ash were presented in Figure 3. Based on Figure 3, it is found that the Zea mays growth in the interaction time 4 weeks showed the better fertility than others interaction time. In addition, the growth of Zea mays on soil and treated soil in order of the most fertile to less fertile as follow : soil + urea SRF 3, urea SRF2, urea SRF1, urea and soil only. The Zea mays with treatment urea SRF3 to be more fertile, with a higher number of leaves and a higher stem.

The effect using SRF at varies time interaction on plant height and number of leaves were shown on Figure 4. Based on Figure 4, it can be seen that within 4 weeks, soil+ SRF3 has optimal growth
and development. This can be seen from the growth of plant height and number of leaves faster than other plants, because the soil nitrogen content is sufficient for the growth of *Zea mays* plants. In soil, fertilizer will release ammonium nitrate ions which will undergo nitrification and produce nitrate ions which can be absorbed by plants [20]. The nitrogen content in the soil can stimulate plant growth, especially stems, branches, and leaves [21].

![Figure 3](image)

*Figure 3.* Growth of *Zea mays* plant on soil (S), soil-urea (SU), soil urea (SRF1), soil urea (SRF2), soil urea (SRF3) with interaction time: (a) 1, (b) 2, (c) 3 and (d) 4 weeks

![Figure 4](image)

*Figure 4.* Effect of interaction time on: (a) the plant height and (b) number of leaves
The nitrogen content of the leaves spurs which acts as an indicator of plant growth in the process of photosynthesis. Even spread of light that can be received by the leaves in the photosynthesis process causes an increase in the assimilation process, where the assimilate will be used as plant growth energy to form vegetative organs such as leaves and plant height.

4. Conclusion

Based on the characteristic results using XRD and FT-IR shows that fly ash can be converted into low grade zeolite material containing minerals, especially zeolite A. The use of SRF ure on Zea mays plants showed better growth than using urea fertilizer without zeolite slow release ingredients. The greater the zeolite component in SRF the better the growth of Zea mays. The growth of Zea mays plants increases in line with the increase in growth time.

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