Hybridization of nitrogen compounds and hydroxyapatite: a slowly released fertiliser for water sustainability

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Abstract. Ammonium sulfate (ZA) and nitrogen-phosphorus-potassium compound (NPK) are nitrogen-rich fertilisers commonly used by farmers. The fertilisers have high solubility in water, decay rapidly in wet soil and decompose into ammonia. Its lead into eutrophication phenomena and its absorption by crop roots becomes less effective. A facile and scalable method is developed to adsorb nitrogen-rich compounds into fish scale based powdered hydroxyapatite for slow-release fertiliser (SRF). Hydroxyapatite (HA) is a material that contains phosphorus and is a well-binding agent of nitrogen. This study is aiming at synthesizing HA from calcium-rich fish scale biowaste using wet-chemical precipitation method and coated the HA particles with ZA and NPK fertiliser. The fertiliser in solid form were combine with HA particles with the ratio of 6:1, and dissolved in aquadest. Total nitrogen content were measured periodically by using percolation method. The nitrogen release of the hybrids was compared to obtain the best kinetics model and it was found that zero order kinetics model was suitable for ZA-HA sample and Kosmeyer-Peppas model was suitable for NPK-HA sample. Vegetative growth of mustard plants were used to measure the effectiveness of SRF, and were found that combination of NPK-HA and ZA-HA were able to enhance up to 17% of the plant growth compare with conventional fertiliser.

1. Introduction

Chemical fertiliser is a key contributor of agricultural intensification. Nitrogen, phosphorus and potassium compound fertilisers promote significant rice plantation yield in Asia [1]. High demand of food production fostering massive utilization of chemical fertilisers. However, only about 70% of the fertiliser nutrients absorbed by the crops, and the rest normally leached through agricultural run-off. The nutrient enrichment goes in enclosed estuaries leads the eutrophication phenomenon. Nutrient rich water pollution found in Asian countries which use great amount of chemical fertiliser such as China [2] and Indonesia [3]. Serious eutrophication manifested by excessive algae blooms in lakes, rivers and oceans, and killed many aquatic animals.

The use of fertiliser is inevitable, however the its utilization should maintain the balance of food-water-energy nexus. Appropriate use of fertiliser by maintaining the rate of nutrients absorption by the crops is essential. Hydroxyapatite (HA) is biomaterial contains rich of phosphorus compounds, could be...
derived from agricultural or aquacultural wastes [4]. The concept of hybrid HA and ZA/NPK (ammonium sulfate/nitrogen-phosphorus-potassium compound) fertiliser is investigated in this study. The HA alone is potential to be used as fertiliser [5, 6]. The combination of HA and traditional fertilisers has at least three advantages, i.e. HA is well-binding agent of nitrogent (from the fertiliser), HA solid particle as porous material acts as adsorber of liquid fertiliser, and the HA itself rich of phosphorus. The pioneering study on the topic can be find elsewhere [7], however this study has two novel aspects, e.g. utilize HA particle derived from fish scale waste, therefore we promotes the use of agricultural waste for agricultural production; and the hybrid fertilisers are NPK and ZA, instead of urea which has already studied. Urea is mainly contains nitrogen, but ZA and NPK contains a more complex subtances. This study are aiming at the investigation on the effectiveness of hybrid NPK-HA and ZA-HA fertilisers to enhance plant growth.

2. Materials and Method
2.1. Materials
HA particles were synthesized from red snapper fish scales using wet chemical precipitation method [8]. Two types fertilisers were used, NPK and ZA (PT Petrokimia Gresik). NPK has nitrogen, phosphorus, potassium and zinc compounds, while ZA is mainly nitrogen and sulfur compounds. Selenium mixture (Merck), NaOH, HCl, H₂SO₄, HBO₃, Whatman 41 filter paper purchased from local chemical supplier.

2.2. Preparation of SRF encapsulated HA
Slow release fertiliser (SRF) encapsulated hydroxyapatite (HA) was synthesized by using previous method [7]. Solid fertiliser and HA particles were mixed by using 6:1 mass ratio, and dissolved in aquades 1:20 (w/v). The solution was then stirred at 200 rpm, 25°C room temperature for 1 hour. The solution was then oven dried at 50°C for 24 hours, and the hybrid solid particles with particle size between 5.76 μm to 132.64 μm were obtained.

2.3. Percolation method
Following the procedure from Kottegoda et al. [7], nitrogen release testing was carried out by using percolation method. A simple and customized percolation testing apparatus was manufactured from cylindric plastic and filled with 0.149 mm sand filter (Figure 1). The percolation test were observed in different time variation, i.e. 120, 240, 360, 480, 600, 720, 840, 960, 1080, 1200 and 3600 s. The distilled water flowed through the cylinder on the rate of 3 mL/min. The percolate then tested for nitrogen content using Kjehdhal method. Four types of samples with no replication were tested: pure fertiliser samples and HA encapsulated fertiliser samples.

![Percolation test apparatus.](image)

**Figure 1.** Percolation test apparatus.
2.4. Measurement of total nitrogen
After percolation testing, it was then analyzed by the Kjeldahl method [9]. There are three stages in the Kjeldhal method. The destructive process, in which 1 mL of percolation results was taken and placed in a Kjeldhal flask and added by 12.5 mL of concentrated H$_2$SO$_4$ (98%) and 0.5 g of selenium mix. Then the sample was extracted on the digestion device for 1 hour at a temperature level 10 from the tool (~420°C) after finishing the sample is cooled at room temperature for more than 1 hour. Then continued with distillation stage, the 250 mL Erlenmeyer flask was first filled with 20% boric acid as much as 20 mL and 3 drops of methil red indicator. Before distillation, the sample was first added with 10 mL distilled water and 70 mL 30% NaOH into the pumpkin Kjeldahl (pumpkin destruction). After that, the distillation process, in which the sample was placed in a distillation unit and run for 5 minutes. The distillation extracts were stored in Erlenmeyer which has boric acid and MR indicator until the color of boric acid changes from red to yellow. Following the titration using 0.1 N HCl until the color turned into orange color. After that, the calculation of N levels is carried out with the following formula:

$$\%N = \frac{(V_{HCl} - V_{blank})DF[HCl] (MW_N \times 100\%)}{W_{sample} \times 1000}$$  \hspace{1cm} (1)

where $V_{HCl}$ is net volume of HCl, $DF$ is dilution factor, $MW_N$ is molecular weight of nitrogen, $W_{sample}$ is weight of the sample.

2.5. Testing of surface area
BET (Brunauer-Emmett-Teller) method was used to measure adsorption-desorption isotherms of hydroxyapatite particles.

2.6. Fertiliser performance
Fertiliser performance has been evaluated on mustard plants growth by using indicator of height of mustard plants, diameter of stem, and number of leaves. The result of fertiliser was observed every 7 days, start from plants aged 1 week until the 5 weeks.

3. Results and Discussion
3.1. Release of nitrogen using percolation method
Release of nitrogen using percolation method is shown in Figure 2.
As shown in Figure 2, within 3600 seconds the pure NPK sample can release nitrogen of 0.71 parts (10.7% of total nitrogen 15%). Then in pure ZA samples, within 3600 seconds can release nitrogen of 0.85 parts (23.08% of total nitrogen 26.95%). Whereas the SRF fertiliser NPK+HA can be released by 0.42 parts (6.34% of total nitrogen 15%) and then ZA+HA sample, in 3600 seconds, it can release nitrogen 0.16 parts (4.23% of total nitrogen 26.95%). This can prove that fertiliser encapsulated by hydroxyapatite can slow down the rate of nitrogen release. This research has been in accordance with previous research [7] which explains that the use of hydroxyapatite in agriculture can be used as fertiliser to release slowly.

3.2. Release kinetics of nitrogen

In this study, four types of nitrogen release kinetics models were used: zero order kinetic, first order kineticic, Higuchi model and Korsmeyer Peppas model. The percolation data were plotted using a linear curve, and obtained R square values. The models are shown in Figure 3.

![Figure 3. Release kinetics of nitrogen by using four kinetic models: (A) Zero order kinetic, (B) First order kinetic, (C) Higuchi model, and (D) Korsmeyer-Peppas model.](image)

As shown in Figure 3, the best kinetics model in the NPK-HA sample is Korsmeyer-Peppas, and the best kinetics model in ZA-HA sample is Zero order kinetic. If the release kinetics follow Korsmeyer-Peppas, the release process that occurs is through the diffusion and erosion mechanism. Then if the release kinetics follows Zero order model, the release process is constant with time.
3.3. Surface area analysis

Surface area is an important indicator in knowing how well a material can be used as an adsorbent. The result of surface area from the BET test on 600°C HA samples is 24.28 m²/g, while NPK+HA sample, the resulting surface area is 7.24 m²/g. Moreover in the 800°C HA sample, the resulting surface area was 25.3 m²/g and in the ZA+HA sample, the resulting surface area is 9.834 m²/g. Based on these results, it can be seen that the surface area of HA has decreased along with the addition of adsorbate [7,10]. To be a good adsorbent, HA must have a minimum surface area of 5m²/g. The pores produced from 800°C HA samples were 8.637 Å using the Horvath-Kawazoe method, and when using the Saito-Foley method, the resulting pore was 16.471 Å. Whereas in 600°C HA samples, pores were produced using the Horvath-Kawazoe method which is 1.834 Å, and when using the Saito-Foley method, the resulting pore is 2.261 Å. Pore size distribution is a very important property for an adsorbent [11].

3.4. Fertiliser performance based on vegetative growth: height of mustard plants

The fertiliser performance on vegetative growth of green mustard plants were shown in Figure 4 below.

![Figure 4. Growth of mustard plants based on different fertiliser condition.](image)

As shown in Figure 4, the plant height for 35 days for treatment using ZA+HA fertiliser growth of green mustard plants was better than treatment using only pure ZA fertiliser and not using fertiliser. The treatment without using fertiliser results is 136 mm, then the treatment uses pure ZA fertiliser of 171.8 mm, on ZA+HA of 195.6 mm, the pure NPK treatment was 150.6 mm and the treatment used NPK+HA fertiliser was 176 mm. According to Kottegoda et al. [7], where ZA compound fertiliser is the biggest constituent, the N element is 21% and the S element is 24%. The level of total nitrogen of ZA fertiliser is very important to know because it is used as a comparison of nitrogen during the release of nitrogen in the fertiliser. N content of ZA fertiliser in the market with several trademarks ranges from 25.38% - 26.95%.

3.5. Fertiliser performance based on vegetative growth: diameter of stem

The fertiliser performance on mustard plants stem diameter were shown in Figure 5.
As shown in Figure 5, the stem diameter of mustard plants without using fertilisers from Day 7 to 35 yielded 3.4 mm, while the addition of pure ZA fertiliser resulted in a stem diameter of 5.2 mm and adding ZA+HA fertiliser resulted in a stem diameter of 6.4 mm. When using pure NPK fertiliser, the stem diameter reached 4.4 mm, and when using NPK+HA fertiliser resulted in a stem diameter of 5.4 mm. The growth is expected can be increased with tall plants, so the larger the diameter of the trunk, the higher the plant. According to Sumida et al. [12], the relationship on the stem height and diameter of the stem indicates that the larger diameter of stem promotes the higher stem growth.

3.6. Fertiliser performance based on vegetative growth: number of leaves
The fertiliser performance on mustard plants number of leaves were shown in Figure 6.

As shown in Figure 6, the plant without fertiliser after 35 days grew 5.4 strands, while pure ZA fertiliser produced 6 strands and in ZA+HA fertiliser produced 8.6 strands. By using pure NPK fertiliser produced 6.4 strands and adding NPK+HA produced 7 strands. HA is again proved promoting growth in the mustard plants, either as stand-alone HA particles or combine with conventional fertiliser.
4. Conclusions
NPK+HA and ZA+HA fertilisers have a slower rate of nitrogen release compared to pure NPK and ZA fertilisers. In 3600 seconds, NPK+HA fertiliser released 0.42 parts of nitrogen, ZA+HA fertiliser released 0.16 parts of nitrogen, NPK fertiliser released 0.71 parts of nitrogen and ZA fertiliser released 0.85 parts of nitrogen. It is concluded that slow release fertiliser (SRF) encapsulated hydroxyapatite (HA) is able to release nitrogen slowly compared with without HA. Moreover, based on the observations on vegetative growth of mustard plants, e.g. height of plants, diameter of stem and number of leaves, slow release fertiliser (SRF) encapsulated hydroxyapatite (HA) has a positive impact to plant growth, as compared with traditional fertiliser. Therefore, slow release fertiliser (SRF) encapsulated hydroxyapatite (HA) could contribute to improve production of crops, while maintaining water sustainability. However, the effect of HA on crops with fruits should be investigated further.

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