Evaluation of natural zeolite as adsorbent material for the recovery of nutrients from manure wastewater

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Abstract. Recovery of nutrients from the manure wastewater has a potential for cost saving in the treatment process. Utilizing the recovered nutrients help reducing the amount of chemical fertilizer in an agriculture. The objective of this research is recovering nutrients from pig farm wastewater via the adsorption of various zeolite and this zeolite compound as organic fertilizer in growth of Green mustard. The objective of this research is optimizing the absorption of the total nitrogen and phosphorus of zeolite under various parameters, including the zeolite weight, the adsorption time, Azotobacter addition and the aeration. Results showed that the rate of 30g zeolite with supplementation of 5ml microbial was aerated in 72 hours for the best efficiency. After 21dates of growth, combination of chemical fertilizers and organic fertilizers mentioned the great products on both height and total harvested weight.

1. Introduction
In recent years, the rapid economic development of the livestock industry has led to a large amount of Pig manure wastewater, which generally contains high concentrations of nutrients such as total nitrogen (TN) and total phosphate (TP). If these compounds present in significant quantities of surface water sources such as rivers and lakes. At this point, algae and other microorganisms can use these compounds to overproduce in water sources. Consequently, eutrophication occurs and decline in dissolved oxygen in the water, causing water to be toxic to fish [1] and the air environment occurs the unpleasant smell. Therefore, reducing the nutrients nitrogen and phosphorus in pig waste water is necessary before discharge around livestock farms to prevent surface water pollution. This activity seems the most economical method for wastewater treatment [2]. However, microbial activity in biological treatment systems can be significantly inhibited by high concentrations of ammonia nitrogen (NH3) in the Pig manure wastewater [3]. Thus, it leads to the decreased efficiency in biological processes.
Some physical or chemical methods can solve this problem, an example is stripping ammonia [4]. There are struvite precipitation [5], zeolite adsorption [6], membrane separation [7] and microwave radiation [8], being selected. For more detailed, struvite stone formation method has proven effective in simultaneous recovery of TN and PT from Pig manure wastewater [9]. Due to the simultaneous presence of TN and PT in wastewater $\text{Mg}^{2+}$, $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ can crystallize to form struvite stones (MgNH4PO4.6H2O) when magnesium salts are added to the Pig manure wastewater, and then level of pH increases to 8-9. However, the concentration of TN in Pig manure wastewater exceeded TP, TN removed by crystallization of $\text{Mg}^{2+}$, $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ are very low at same mol concentration. If results can achieve the high removal efficiency of TN, additional phosphate salts will be added this water pollution, this process will significantly increase treatment costs. In particular, reducing TN by zeolite's adsorption is paid attention with high efficiency because of its low cost and simplicity [9]. Zeolite is crystalline of aluminosilicate mineral consisting of three-dimensional porous micro-SiO44- and AlO45- tetrahedral links via oxygen atoms. It usually represents a high selectivity for ammonium and metal ions, it is used as an ion exchange device in softening and water purification [6].

Clays and modified clays along with zeolites are also being used for environmental cleanup [10] [11]. These materials have recently become very popular due to their low cost of production, easy availability, and multiple uses. Thus, clay minerals and zeolites are frequently used for preparation of controlled release of fertilizers, pesticides, and herbicides [12-14]. At another aspects in an agricultural production, it is an increase of the demand and prices of fertilizers, reuse the nutrients in the wastewater serving agriculture, being encouraged to apply to reduce the use of fertilizers. Recent study showed that an important technique to improve the yield of crops is controlled release of fertilizers and pesticides. A huge gap exists between the nutrient release and plant uptake, which contributes to the lower efficiency of fertilizer nutrient. Similarly, the less release fertilizer lead to less release of pesticides may bring to less pollution of the natural environment. The advantages of these controlled releases of fertilizers and pesticides are decreasing loss rate, sustainable supply of pesticides and nutrients, lower application rates, and minimization of adverse effects to the environment [12, 15]. In addition, zeolites and clay minerals can be utilized as soil conditioners to improve the soil’s physical properties [16]. Zeolites content in soil can be a useful factor for organic carbon sequestration due to the role of zeolite in aggregate formation by providing a sufficient amount of base cations [17, 18] and supplying base cations to highly weathered tropical soils has also been reported [19].

In the others hand, Azotobacter has long been well recognized as a potent, free living nitrogen fixer especially for agricultural crops [20]. However, some of the harsh conditions such as high-temperature environment will inhibit the activity or lethal. Keeping and storing microbial cells in adsorbents to protect them from adverse conditions in the environment is currently getting wide attention due to the advantages it offers. These include stimulation of microbial metabolism, protection of cells from unfavorable agents, and preservation of their physiological activity [21]. Immobilization of microbial cells by adsorption is low cost, simple, and avoids the stressful cell treatment [22], as compared to other methods based on mechanical cell incorporation and chemical binding. It is also a universal method of preservation of the cells in physiologically active state [23]. Among a wide range of adsorbents available, the unique physical and chemical properties of natural zeolites especially high porosity and large surface area have made them useful for the immobilization of microorganisms [24] and also in agriculture as slow-release fertilizers [25]. Therefore, the use of suitable zeolite combination will bring many different benefits, the first is the treatment of wastewater, recover nutrients and be storage houses for microorganisms with beneficial habitat.
Hence, zeolites and clay minerals showed a huge potential not only to enhance nutrient use efficiency through controlled release as well as environmental remediation from toxic organic and inorganic pollutants but also effective to conserve soil moisture. To be able to use zeolite appropriately for treating manure wastewater and bringing benefits towards suitable for maintaining agricultural sustainability on a long-term basis, the study aim of this research is that testing the ability to adsorb nutrients in manure wastewater under various conditions, especially the ability to coordinate with Azotobacter to test and compare with other fertilizers to evaluate the effectiveness of Green mustard growth in experimental condition.

2. Materials and methods

2.1. Research materials

Pig manure wastewater was taken from pig breeding farm of University of Agriculture and Forestry in Ho Chi Minh City (Viet Nam). The wastewater will be mixed in a large basin, the sample will be analyzed the total nitrogen, phosphorus and microorganisms. For determination of total N-concentration using kjeldah method (ASTM E258 – 07, 2015); total P-concentration use the sample digestion method (TCVN 8563: 2010). Seeds of Green mustard, Zeolite, organic fertilizers and chemicals was purchased commercially.

| Content | Total N(%) | Total P (µg/ml) | pH | EC (µs) |
|---------|------------|-----------------|----|---------|
| Concentration | 0.07 | 136.838 | 6.89 | 1911 |

Zeolite material is composed of about 80% clinoptilolite with minor clay (mont-morillonite), celadonite, un-reacted volcanic glass and occasional crystalloclastic particles. These characteristics are reflected in the bulk rock chemistry, recorded as oxide percent, K2O 1.90–5.35, CaO 1.86–3.94 and Na2O 0.20–1.21) [26]. Prior to use, the rock was crushed to fragments ranging in size from 0.08 mm to 2.5 mm; no other treatment was required.

There are several characteristics of Azotobacter bacteria as free nitrogen fixation characteristics, growth stimulation, supplementation of zeolite for the production of fertilizers are cultured with N-free LG medium [27] including Glucose, K2HPO4, KH2PO4, MgSO4.7H2O, CaCl2.2H2O, FeCl3.6H2O and yeast extract.

2.2. Experimental Design

E2. Investigation of the effect of Azotobacter on absorption efficiency.

Using Zeolite mass and the optimal time from previous experiments, supplying 5ml medium containing Azotobacter, for the control sample will not supplying the medium containing Azotobacter. The fluid containing Azotobacter strain with concentration of 107 was added in each experimental samples, being estimated 5ml. Repeated three times each experiment.

E3. Investigate the effect of aeration conditions on absorption efficiency.

Using the Hailea Aerator Air Blower ACO 108 (10w; 25L/min; 0.6kg; 125x70x68 mm) along with the weight, time and 5ml medium containing Azotobacter to optimal all the experiment mentioned above. For the control sample will not using the air blower. Repeated three times each experiment.
Figure 1. Flow chart of the experimental method

**E4. Effectively testing Zeolite fertilizers on broccoli and comparing with the other fertilizer products.**

The experiment arrange in to the block style randomly, 3 time repeated with different fertilizing (samples):
- NT1: Without fertilizing.
- NT2: Combine organic fertilizers and chemical fertilizers.
- NT3: Zeolite fertilizer.
- NT4: Combination of Zeolite and composted coffee shell.
- NT5: Combination of organic fertilizer and Zeolite.

The experiment was arranged following the above above with small crushed soil, dried it 2 to 3 days and then put into the styrofoam box having a hole at the bottom of the barrel. Total all the experiment barrels: 4 x 3 = 12 barrels. The acreage of each barrel: 0.465 x 0.33 = 0.15m$^2$. The distance between rows is 20cm, space between each trees is 15cm. Fertilizer time: fertilizing before seeding, fertilizing after seeding 7 days. The monitoring indicators include the height of each tree, the number of leaves of each tree and the fresh weight of each tree. Data were analyzed statistically using analysis of variance (ANOVA) and differences among the means were determined for significance at $P \leq 0.05$ using Duncan’s multiple range test (by SPSS software).

3. Results and discussion

3.1. Effect of weight and time on adsorption efficiency of Zeolite

From figure 2A, results showed that an experiment with 10 g Zeolite for 24 hours had 0.0704% as the highest total nitrogen content, it only lower than the total input nitrogen content of 0.0743%, even higher than control.
Results showed the adsorption time increased, the total nitrogen content in the pig manure wastewater began to decrease gradually. At 72 hours presented that the total nitrogen content was lower than control, if the amount of Zeolite increased 20 gram, the total nitrogen content in pig manure wastewater gradually decreased during the experimental time. Supplementation of 20g Zeolite in 72 hours, total nitrogen content was reduced to 0.0554%, being lower than control. When an amount of Zeolite increased 30g, the total nitrogen content in the pig manure waste was reduced significantly at the experiments of 30 g Zeolite in 24 hours, 48 hours, 72 hours, this total nitrogen content in the pig manure wastewater was lower than control. The experiment results of 30 g Zeolite in 72 hours showed the total nitrogen in pig manure was reducing to 0.0530%, lower than 0.0743% of the total nitrogen input and also lower than 0.0606% of control.

The amount of the total nitrogen in the pig manure waste water decreases, it will be explained by degraded by metabolism or adsorbed by Zeolite. Comparison between results of input treatments and control found that the amount of total nitrogen in pig manure waste still decreased without the addition of Zeolite. This phenomenon proves that nitrogen is likely to be degraded during the transformation process, however, the addition of 30 g Zeolite in 72 hours is lower than control. It means that the reduced amount of total nitrogen is conducted by the Zeolite adsorption.

From figure 2B, there are fluctuation of the total phosphorus content between experiments. In experiment 1, supplemented with 10g Zeolite showed an amount of total phosphorus was lower than the control. When the amount of Zeolite increased 20 g in 24 hours, the total phosphorus in the pig manure waste increased, being higher than control. But this process keep continuing to 48 hours, the total phosphorus in the pig manure waste was lover than control. At this point, increasing the amount of Zeolite to 30 g Zeolite in 72 hours the total phosphorus concentration in the pig manure wastewater was 143,495 µg/ml, being higher than 136,838 µg/ml of the input of pig manure waste. Therefore, it can not use the total phosphorus concentration to conside the absorption efficiency of Zeolite for phosphorus by weight and time.

3.2. Effect of Azotobacter on the adsorption efficiency of Zeolite

Azotobacter bacteria have a good ability to fix nitrogen, it is a reason why supplementing Azotobacter bacteria impact on the adsorption effect of Zeolite, being the research factor in this study. We conducted two experiments, an experiement 1 did not have Azotobacter bacteria, an experiement 2
supplemented with 5 ml fluid containing *Azotobacter* bacteria. Final results were shown in following chart.

![Figure 3. Total nitrogen (A) and Total phosphorus (B) in the pig manure wastewater, containing *Azotobacter* bacteria in 72 hours](image)

Results in figure A showed that the experiment has 30 g Zeolite, 5 ml fluid containing *Azotobacter* bacteria in 72 hours, this result presented the total nitrogen content in pig manure waste around 0.049%, being lower than 0.074% the total nitrogen of input from pig manure waste & remaining experiments. Statistical results at significant levels (P <0.01) show meaningful differences. This result proved that *Azotobacter* bacteria affect the nitrogen adsorption efficiency of Zeolite. Prachi Joshi's research shows that zeolite is an extremely suitable material for carrying microorganisms, especially *Azotobacter*. The results also showed that zeolite hold the cells in the root root of plants and to protect them under stressful conditions such as contact time or pH change \[28\]. Therefore, it is possible that these bacteria also make the synthesis and storage of nitrogen in zeolite more favorable.

Results in figure B showed that the total phosphorus in the pig manure wastewater fluctuated without the experimental rules. Primary results of total phosphorus was 136,838 µg/ml lower than the experiment having 30 gram of Zeolite, 5 ml fluid containing *Azotobacter* bacteria in 72 hours. Phenomenon illustrated that the total nitrogen in pig manure waste usually decreased when the experiment supplements Azotobacter bacteria, but the total phosphorus increased dramatically compared another remaining experiments. So, *Azotobacter* did not affect the phosphorus absorption of zeolite.

### 3.3. Effect of aeration on the absorption efficiency of Zeolite

Aeration is a process that oxygen is supplied in this experiment, the aeration provide a good environment for working the healthy aerobic microorganisms. This process support the dissolves nitrogen and phosphorus to be more easily absorbed. Therefore, research of the aeration condition was is essential to know the effect on the absorption efficiency of Zeolite.

Both experiments also added 40 g Zeolite, 5 ml fluid containing *Azotobacter* bacteria in 72 hours, an experiment 1 had an aeration condition and experiment 2 did not have an aeration condition. Results showed that total nitrogen in the experiment 1 with an aeration condition was 0.022%, being lower than 0.034% of experiment 2 and 0.449% of control. Results proved that that aeration has a great effect on the nitrogen adsorption efficiency of zeolite. Evaluated results of phosphorus showed
that the experiment with aeration in 72 hours gave 56.785 µg/ml of the total phosphorus of pig manure waste, being lower than 263.38 µg/ml of primary experiment and another experiments. The statistically significant (P<0.01) showed differences in statistical significance between experiments. Results meant that the aeration condition greatly affected the phosphorus adsorption efficiency of zeolite.

Figure 4. Aeration condition effecting on Zeolite adsorption efficiency in 72 hours for total nitrogen (A) and total phosphorus (B) in the pig manure wastewater

3.4. An effectiveness assessment survey of Zeolite on Green mustard

An assessment survey of factors affecting on the adsorption efficiency of Zeolite in the laboratory scale. We conducted a synthesis of experimental factors to create fertilizer of Zeolite products and their quality as follows.

Figure 5. Process of creating zeolite fertilizers [A] Pig manure water, [B] Zeolite supplementation and environment containing Azotobacter; [C] Continuous aeration; [D] Finished Zeolite
Carefully mix pig manure wastewater
Styrofoam box (50 liters)
Slowly put zeolite in this solution (weight 2kg)
Add 250 ml of environmental solution containing Azotobacter
Keeping the aeration condition in 72 hours
Naturally dry by evaporating
Dry powder
Zeolite fertilizers

Figure 6. Diagram of experimental production process of zeolite’s fertilizer

Table 2. Substances composition presenting in zeolite’s organic fertilizer

| Component | Unit | Concentration | Component | Unit | Concentration |
|-----------|------|---------------|-----------|------|---------------|
| N         | %    | 1.176         | K         | %    | 0.49          |
| P         | %    | 1.12          | pH        |      | 8.62          |

Experiment was carried out in styrofoam box 65x45cm with 4 experimental category (n=3), the fertilizer was prepared before planting, top dressing after 12 days of planting. The amount of fertilizer was used around 3% of the amount of soil at styrofoam box. Evaluated results for height indicators in this experiment showed that there was no difference in the first 5 days, and then there were significant differences, keeping to the end of experiments. The ability of fertilizers on Green mustard was obtained in Table 3:

Table 3. Fluctuation of Green mustard height in experiments

| Experiments                                      | Growth times |
|-------------------------------------------------|--------------|
|                                                 | 5            | 12           | 18           | 21           |
| No fertilizer (NT1)                             | 6,017 ± 0,25 | 7,795 ± 0,65 | 11,000 ± 0,58 | 12,958 ± 0,76a|
| Organic + chemical fertilizers (NT2)            | 6,850 ± 0,09 | 11,383 ± 0,63| 19,775 ± 0,07 | 22,208 ± 1,34b|
| Zeolite fertilizers (NT3)                       | 6,383 ± 0,10 | 7,792 ± 0,55 | 12,842 ± 1,04 | 16,750 ± 0,63b|
| Zeolite fertilizers + compost of coffee shell (NT4) | 6,483 ± 0,08 | 8,108 ± 0,35 | 14,575 ± 1,99 | 15,875 ± 1,07b|
| Organic fertilizers + zeolite (NT5)             | 6,367 ± 0,19 | 10,307 ± 0,79 | 17,087 ± 0,41 | 19,667 ± 1,06a|

Following values have the same character with no statistically significant difference (P <0.05).
Green mustard's height gradually increased from 12 to 21 dates after planting, the highest was experiment 2 from 6,850 to 22,208 cm, which lowest is experiment 1 (control) from 6,017 to 12,958 cm. Statistical results (P <0.05) also showed that there were significant differences between treatments. This data presented that this Zeolite provided nutrients for the plant height development.

Table 4. Fluctuation of Green mustard leaves (number of leaves)

| Experiments                              | Growth dates |
|------------------------------------------|--------------|
|                                          | 5            | 12           | 18           | 21           |
| No fertilizer (NT1)                      | 6,667 ± 0.29 | 8,167 ± 0.52 | 9,833 ± 0.14 | 11,250 ± 0.75 |
| Zeolite fertilizers (NT3)                | 6,833 ± 0.14 | 8,917 ± 0.14 | 9,333 ± 0.29 | 10,833 ± 0.63 |
| Zeolite fertilizers + compost of coffee shell (NT4) | 6,250 ± 0.25 | 8,000 ± 0.25 | 9,333 ± 0.72 | 10,917 ± 0.52 |
| Organic + chemical fertilizers (NT2)     | 7,000 ± 0.00 | 9,083 ± 0.14 | 11,333 ± 0.63 | 13,167 ± 0.38 |
| Organic fertilizers + zeolite (NT5)      | 6,833 ± 0.29 | 8,833 ± 0.29 | 10,750 ± 0.25 | 11,917 ± 0.63 |
| Zeolite fertilizers + compost of coffee shell (NT4) | 8,200 ± 0.34 |

Following values have the same character with no statistically significant difference (P <0.05).

Table 5. Harvested weight of Green mustard in experiments

| No | Experiments                              | Weight (gram/plant) | No | Experiments                              | Weight (gram/plant) |
|----|------------------------------------------|---------------------|----|------------------------------------------|---------------------|
| 1  | No fertilizer (NT1)                      | 4,708 ± 0.73       | 4  | Zeolite fertilizers + compost of coffee shell (NT4) | 8,492 ± 1.62       |
| 2  | Organic + chemical fertilizers (NT2)     | 24,758 ± 2.73      | 5  | Organic fertilizers + zeolite (NT5)       | 17,717 ± 2.98      |
| 3  | Zeolite fertilizers (NT3)                | 8,200 ± 0.34       |    |                                          |                     |

Following values have the same character with no statistically significant difference (P <0.05).

The results compared with Alami's study showed that the height of the samples was approximately equal, but the number of leaves was 1.5 times more superior [29]. Table 4 showed that the variation in the leaves number had the changes in each growth stages and there were the poor absorption of the nutrient in the early stages. In the mature stage, Green mustard was accustomed to the life environment, roots absorb nutrients in different fertilizer environments, leading different results. The number of true leaves in experiments increased gradually from 12 dates and reached the highest value.
at 21 dates. In the day 21, Green mustard in experiment 2 had the highest level of development from 6 leaves to 13 leaves, it means statistically significant for experiment 1, experiment 3, experiment 4 and except experiment 5 (Table 5). All results were statistically significant (P <0.05) and this results showed that Zeolite fertilizer has the effect of enhancing leaf development of Green mustard.

Plant productivity is constituted by many factors such as weight, density, pest situation. In particular, the weight of plant obtained from factors as height, number of leaves. In addition, the yield of Green mustard depended on the soil, climate and weather. The plant ability is evaluated how to absorb nutrients and especially the source of fertilizer.

Average weight of Green mustard was significantly different (P <0.05) in all experiments. Results showed that the weight of Green mustard grown in experiment 2, reaching the highest value with significant differences for the remaining experiments. This is true of the results of Bandyopadhyay et al’s study that the proper combination of chemical fertilizers and organic fertilizers will bring superior results [30]. In this case, experiment 3, 4 and 5 were equivalent and the lowest value is experiment 1. Thus, results showed that Zeolite fertilizer have an effect on increasing the plant yield. However, more research is needed on the appropriate dosage or joint use with a small amount of chemical fertilizers to achieve the best results.

4. Conclusion

Experimental results showed that zeolite has the ability to adsorb and recover nutrients (N, P) in pig manure wastewater. It means that Zeolite can be used in the first stage of the process of treating pig manure wastewater in order to reuse the nutrient supplying for plants. Results proved that the experiment had 30g zeolite, 5ml fluid containing *Azotobacter*, the aeration condition in 72 hours to provide the best nutrient absorption effect. The analysis showed that zeolite adsorption is considered to compost, relating to the criteria of N, P, K. For more detailed, this study needs to repeat several time to explain benefits of zeolite for the environment in livestock wastewater treatment and the potential fertilizer for agriculture.
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