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EFFECT OF SURFACTANT MODIFIED CLINOPTILOLITE ADDED PROPAGATING SUBSTRATE IN THE GROWTH OF *Clinancathus Nutans*

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Abstract Nitrogen (N), phosphorus (P) and potassium (K) nutrients are important for plant growth especially for herbal plants. N is essential for leaf growth, P is crucial for rooting development of the plants while K is important for fruit and flower development of plants. Zeolite (clinoptilolite) cannot adsorb anions such as phosphate (PO_4^{3-}) and nitrate (NO_3^-) which vital for the plant growth because of its negative charge. Hence, an experiment was carried out to modify clinoptilolite with cationic surfactant, hexadecyltrimethylammonium-bromide (HDTMA-Br) producing surfactant modified clinoptilolite (SMC) which later then added to propagating substrate to form controlled release propagating substrate (CRPS) which can hold and control the anion and cation release. The release behaviour of PO_4^{3-}, NO_3^- and K^+ from CRPS was studied for ten days. Results showed that, the combination of SMC with 50 g propagating substrate could control the anions and cation release and furthermore enhance the growth of *Clinacanthus nutans* during sowing time. Therefore, SMC is needed to be added in propagating substrate to control the release of nutrients during germination or sowing time.

Keywords Controlled release; Propagating substrate; Surfactant Modified Clinoptilolite; Phosphate; Nitrate

1.0 INTRODUCTION

Nitrogen (N) is one of the crucial elements for optimum crop production. Soil nutrients like nitrogen and phosphorus are often limit the plants growth (Entry and Sojka, 2008). According to Berber and his friends, (2013), nitrate is a form of nitrogen that is provided for plant consumption which is difficult to be adsorbed on soil particles. Consequently, nitrate move in the soil together with drainage water and finally causing leaching. Once N leached out to the underground water, it can pollute the environments. Therefore, improving nutrient use efficiency through increasing nutrient uptake and crop yield is the main concern of agriculture producers and users (Ussiri and Lal, 2013).

Recently, zeolite (clinoptilolite) has been used widely in the agricultural field (Li *et al.*, 2013). Zeolites comprise of three dimensional aluminosilicate structures with cation and water within the channel of aluminosilicate framework (Breck, 1974). Because of this structure, zeolite itself cannot adsorb anions such as PO_4^{3-} which vital for rooting development and keep hold the nutrients within their structure. Fortunately, Yusof and Malek (2009) suggest that zeolite can be modified by cationic surfactants and modify its surface so that it have high affinity to adsorb anion. Cationic surfactant hexadecyltrimethylammonium (HDTMA) have a long chain 16 carbon with permanent positive charge provided by ammonium. When HDTMA brought in contact with clinoptilolite, it selectively exchanges with inorganic cations on the outer surfaces of the zeolite crystals and subsequently forming surfactant bilayer with anion exchange characteristic (Bowman *et al*., 2000). Recent study by Li (2003) showed that modification of zeolite by HDTMA can control the release of nitrate and other anions. Recently, Dionisiou *et al.* (2012) and Bansiwal et al. (2006) also stated that surfactant modified zeolite (SMZ) can be an effective adsorbent for phosphate anions.

Propagating substrate or medium containing the mixture of peat with other substances is commonly used as a substrate or medium for sowing the plant.

Normally, peat is mainly used as growing medium in containers in tree nurseries worldwide for its good growing properties (Heiskanen, 2011). Recent study showed that length of flower bud and number of flowers per plant over their pure medium can be improved by adding zeolite to cocopeat, perlite and leca (Rezaee *et al*., 2013). In addition, it has been reported previously that the effects of different growing media (soil, sand, pumice, perlite and perlite+cocopeat) were studied on growth, oil yield and composition of geranium (Rezaei and Ismaili, 2013).

The purpose of this research is to modify the clinoptilolite with the cationic surfactant quaternary ammonium namely hexadecyltrimethylammonium-bromide, in order to enhance the capability of propagating substrate to hold its nutrient especially phosphate and nitrate. This study covers the effect of SMC added to propagating substrate in order to study the growth performance of *Clinacanthus nutans* as a model plant and the release behavior of nutrients.

2.0 EXPERIMENTAL

2.1 Materials

Zeolite type clinoptilolite used was imported from Indonesia and it was supplied by Provet Group of Companies Sdn. Bhd., Selangor. Modification of clinoptilolite's surface was accomplished using hexadecyltrimethylammonium-bromide (HDTMA-Br), (Merck). Propagating substrate that was used for sowing was imported from Holland (Stender).

2.2 Preparation of Surfactant Modified Clinoptilolite (SMC)

Surfactant modified clinoptilolite (SMC) was prepared by contacting natural zeolite clinoptilolite with hexadecyltrimethylammonium bromide (HDTMA-Br) solution. SMC was prepared by mixing 10 g clinoptilolite with 200 mL of HDTMA-Br solution, 4 mmol/L. Then, the mixture was stirred by using magnetic stirrer overnight. The mixture was filtered through 125 mm Advantec filter paper. The solid residual of SMC was dried in oven at 80 ºC overnight. The dried SMC was then ground by using mortar and pestle to form powder.

2.3 Preparation of Controlled Release Propagating Substrate (CRPS)

To prepare controlled release propagating substrate (CRPS), different amount of SMC (1 g, 7 g and 15 g) were mixed evenly with 50 g of propagating substrate and it was then homogenized to ensure the even distribution of SMC in the propagating substrate.

2.4 Experimental Setup for Controlled Release Study

Table 1: List of samples for controlled release study

Sample	Description
P	Control (Peat 50 g)
C7	Peat 50 g + Clinoptilolite 7 g (without surfactant)
SMC1	Peat 50 g + SMC 1 g
SMC7	Peat 50 g + SMC 7 g
SMC15	Peat 50 g + SMC 15 g

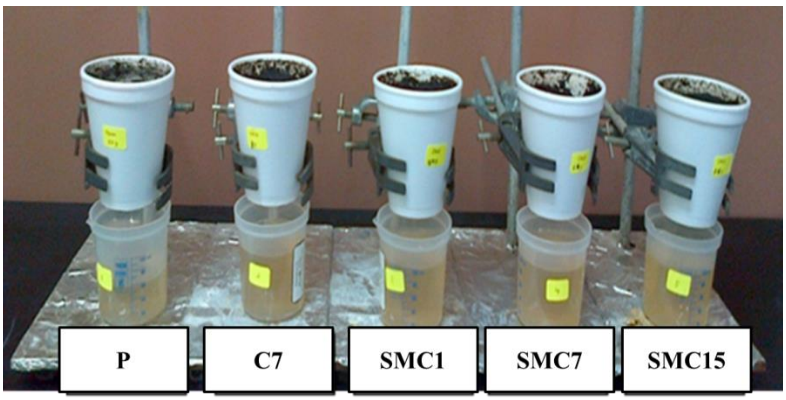

Figure 1 Experimental setup for the controlled release study

The experiment was setup as shown above by using retort stand, polystyrene column with 4×0.5 cm diameter of hole at the bottom and 100 ml plastic beaker. 50 g of samples (Table 1) were placed in the polystyrene column.

Sample in the column was loosely packed and was watered by 100 ml of tap water every day. Columns were permitted to drain for 24 hours before collecting the leachate (Entry and Sojka, 2008). The measure from bottom of retort stand to bottom of column was 7 cm.

2.5 Data collection and Analysis

The data of controlled release study were collected every day for ten days with three replicates.

2.5.1 Photometric Determination as Phospmolybdenum Blue (ortho Phosphate)

This experiment was done to detect the concentration of phosphate release by using NANOCOLOR ortho Phosphate kit.

Test : 1-77

REF : 918 77

2.5.2 Photometric Determination with 2,6-dimethylphenol in Sulfuric Acid / Phosphoric Acid

An experiment was done to detect the concentration of nitrate release by using NANOCOLOR Nitrate kit.

Test : 1-65

REF : 918 65

2.5.3 Photometric Determination as Potassium Tetraphenylborate

The concentration of potassium released was detected by using NANOCOLOR Potassium kit.

Test : 0-45

REF : 985 045

3.0 RESULT AND DISCUSSION

This experiment was done to study the effect of SMC added to propagating substrate in the growth of *Clinancathus nutans* and release behaviour of important nutrients such as nitrate (NO_3^-), phosphate (PO_4^{3-}) and potassium (K^+). Figure 2,3 and 4 show the release of phosphate, nitrate and potassium, respectively from the samples according to Table 1.

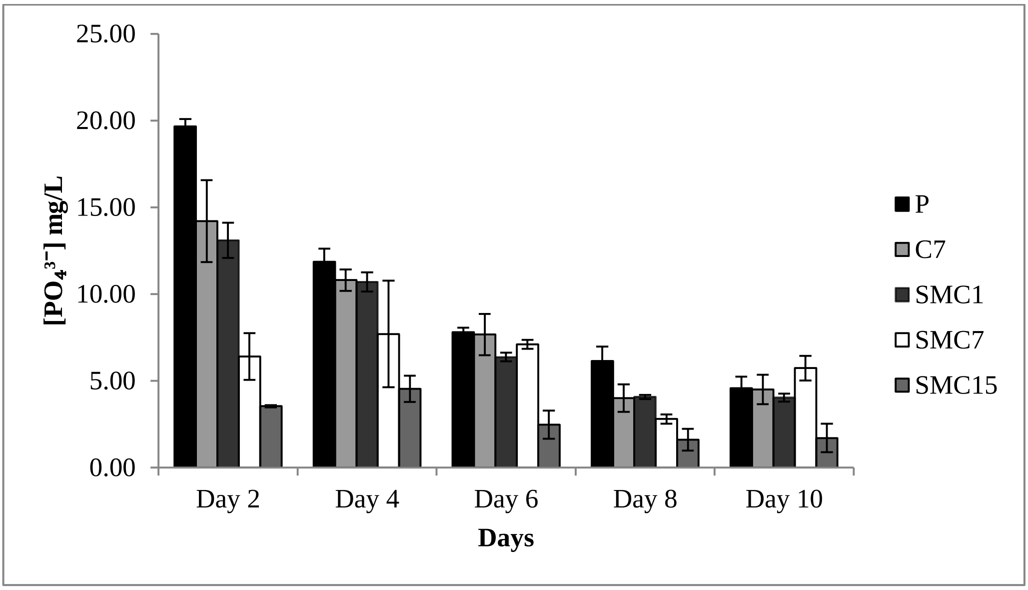

Figure 2 The release of phosphate after the addition of SMC to propagating substrate

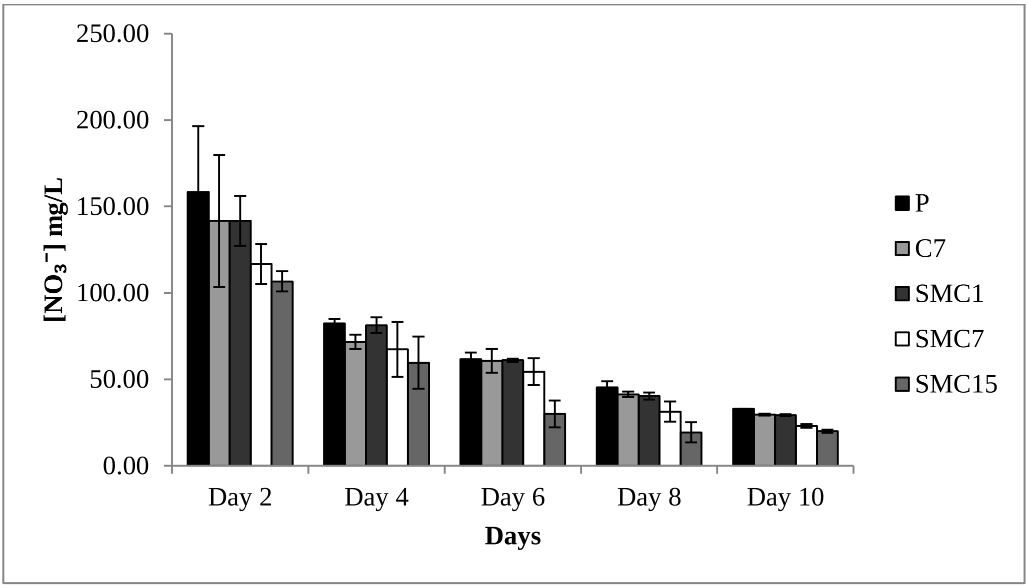

Figure 3 The release of nitrate after the addition of SMC to propagating substrate

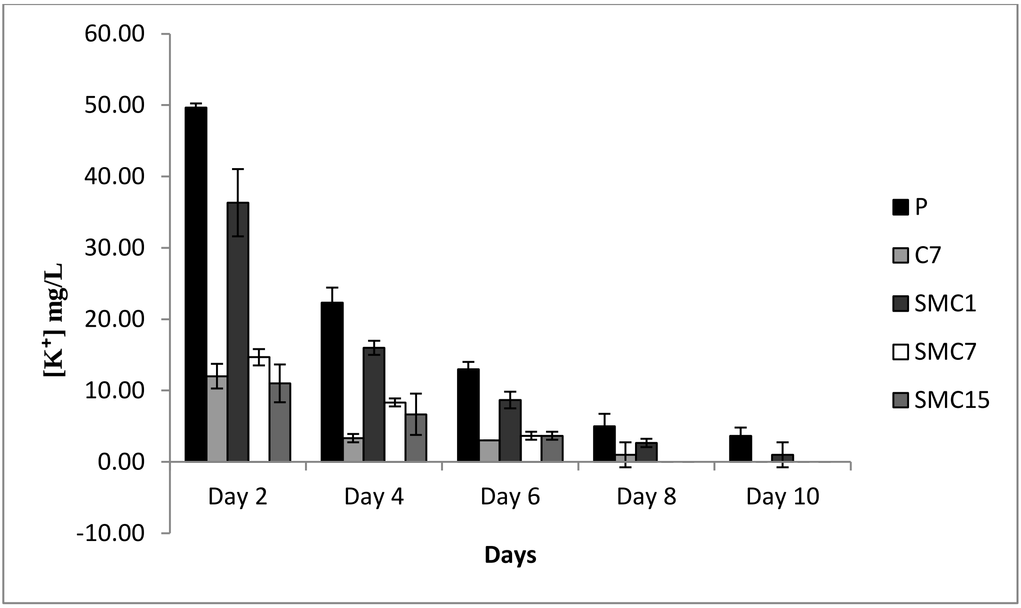

Figure 4 The release of potassium after the addition of SMC to propagating substrate

Figures 2-4 show the results for the controlled release nutrients (phosphate, nitrate and potassium) from each sample as stated in Table 1 at different time and in comparison with control samples (P: without clinoptilolite or SMC / only propagating substrate) and (C7: without SMC / only clinoptilolite and propagating substrate). It was found that the addition of SMC (SMC1, SMC7 and SMC15) in propagating substrate decreased the amount of nutrients released compared to the control sample. Thus, it is proven that the SMC have high affinity to adsorb and hold nutrients in the propagating substrate. This is due to the surfactant bilayer formation of SMC. The positive surface charge of SMC provides site for adsorption of anion such as phosphate and nitrate (Bowman, 1998). Since clinoptilolite itself is negative in charge, it can also hold positive charge nutrient such potassium by ion exchange (Li *et al*, 2013).

Figures 5 and 6 show the growth profiles of *Clinacanthus nutans* after 3 weeks sowing time using the studied samples (Table 1).

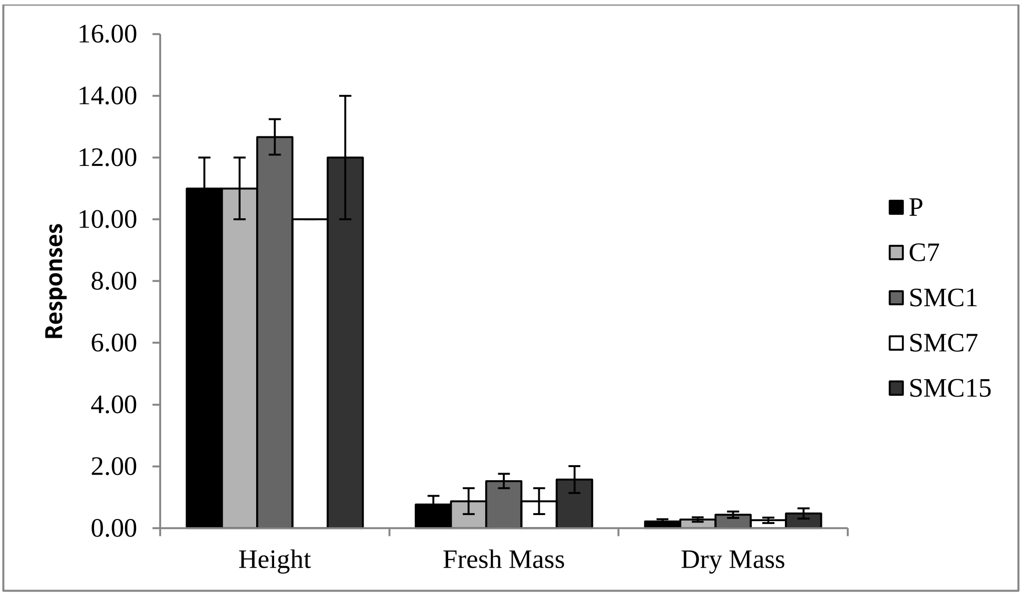

Figure 5 The growth of *Clinacanthus nutans*

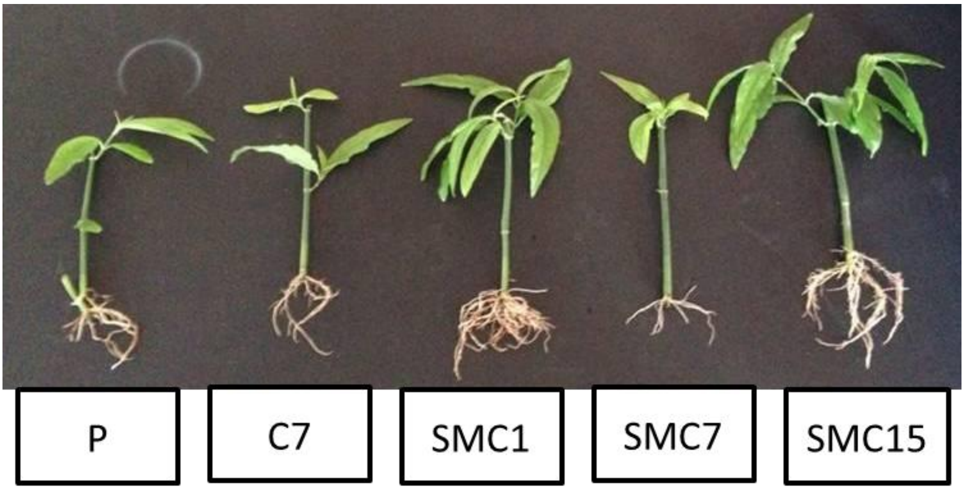

Figure 6 The overall plant condition of *Clinacanthus nutans* after 3 weeks sowing time

It can be seen that the height, fresh mass and dry mass of the plant increased when SMC was added to propagating substrate as compared to control sample. Furthermore, it can be clearly observed from the picture of the plant (Figure 6) that the root development of the plant sowed using CRPS showed increased germination as compared to control samples. This can be explained by the higher amount of P-element (phosphate) in the CRPS compared to only propagating substrate or the mixture of propagating substrate with clinoptilolite. It is known that the root production of plant is stimulated by the present of P in the substrate. The availability of phosphate can affect the root growth. In the present of high phosphate concentration, the growths of plants were more vigorous than those on lower phosphate. Moreover, the total number of root branch and total root system length were greater on higher phosphate concentration (Williamson *et al*, 2001) thus it will increase in the height, fresh and dry mass of the plants.

4.0 CONCLUSION

It can be concluded that the use of controlled release propagating substrate (CRPS) is important during germination or sowing time since it can control and retain important nutrients that needed by plants such as phosphate, nitrate and potassium release which all of the nutrients are necessary for better plant growth and faster the time for root production. At the same time, the substrate also can retain and hold other trace element either cation or anion in CRPS simultaneously.

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