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Full Length Research Paper

Impact of Nitrogen Fertilizer (Encapsulated Urea Fertilizer) in Process of Controlled-Release Their Effect on Growth of Chinese Kale (*Brassica alboglabra* Bailey)

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The project of this work was to determine the effects of encapsulated urea fertilizer (EUFs) on plant growth. Urea was applied as nitrogen (N) which widely used in agriculture as a common source of N in solid form using at rate of 30 kg/ha. Studies carried out in a greenhouse have found that EUFs increasing fresh weight, root fresh weight, stem dry weight and root dry weight of kale plant. Improved understanding of the releasing behavior of controlled-release fertilizer was used Fick's law model. Impacts of EUFs are strongly effect on biomass and mineral N applications. In various considerations, these EUFs represent good controlled-release and water-retention capacity, being degradable in soil and environmental friendly, could be especially used in agricultural applications.

Keywords: Chinese kale, Controlled-release, Encapsulated urea fertilizer, Fick's law model, Urea fertilizer.

INTRODUCTION

The growth of plant depends on the soil condition, quantity of water, especially the quality of fertilizer. Fertilizers are main factors that limit the development of agricultural production and very important to improve the utilization of mineral nutrients for plants. Nitrogen (N) is the one of nutrient most limiting to crop production and nutrient generally applied in the largest amount. About half of all N used for crop production is applied as urea, $CO(NH_2)_2$ (Claus-Peter, 2011), due to its high N content (46%). Urea belongs to the synthetic group of fertilizers (Ramirez *et al*., 1997; Ramirez-Cano *et al*., 2001). In addition, it is a physiologically important by transforming to nitrogenous product in protein metabolism.

In denitrification process, urea is rapidly hydrolyzed to ammonium carbonate by urease activity. Ammonia (NH_3) is particular concern because it can loss exceed 50% of the N apply (Terman, 1979). Moreover, the NH_3 losses may have negative ecological impact on atmospheric quality and then returning to the ground cause soil acidification (van der Eerden *et al*., 1998), act as a secondary source of Nitrous oxide (N_2O) production (Zaman *et al*., 2008, 2009; Zaman and Blennerhassett, 2010; EPA, 2011). The extremely use of urea resulting in ammonium ion (NH_4^+) accumulation which leads to several problems, such as damage of germination seedlings, nitrite toxicity, and gaseous loss of urea N as NH_3 (Carreres *et al*., 2004; Ball *et al*., 2004; McKenzie *et al*., 2007).

The effective N management involves select coating as application which controls the rate of nutrient release.

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These ways could be able to improve efficiency of N utilization also minimization of environmental hazards, controlled release or slow release fertilizers were applied (Hauck, 1985; Shaviv and Mikkelsen, 1993; Peoples *et al*., 1995; Bockman and Olfs, 1998; Shaviv, 1999). Controlled-release N fertilizer products are intended to slow the release of N into the soil relative to regular fertilizers (Newton *et al*., 2010). Controlled-release fertilizers (CRFs) for urea are made by coating with some active soluble materials (membrane) that serve as a diffusion barrier. The coating materials should be contained hydrophilic properties to take up water for fertilizer transportations possible. On the other hand, it is sufficiently hydrophobic to prevent the disruption of coating wall. Biopolymers, polyvinyl alcohols (PVA) and poly (vinylpyrrolidone) (PVP) have also been approved for using in CRFs that are valued for its solubility and biodegradability (Park *et al*., 2001; Lebrun *et al*., 2004; Qiao *et al*., 2005). The environmentally safe and biodegradable coating materials are expected to be used.

Chinese kale (*Brassica alboglabra* Bailey) is an original Chinese vegetable belonging to the Brassicaceae family. It distributes widely in South China and Southeast Asia, especially in Thailand (Sagwansupyakorn, 1994) and is present in relatively small quantities in Japan, Europe and America. Generally, Chinese kale is grown for its bolting stems as the common edible part, whereas the tender rosette leaves are also widely consumed. It also exhibits high nutritional values (He *et al*., 2002).

In this work, PVA and PVP were developed as coating materials came to be Encapsulated Urea Fertilizer (EUFs) that were designed for preventing the nutrient loss and controlling rate of release. The releasing behavior was described by Fick's law model (Al-Zahrai, 1999; Peng *et al*., 2006). The objectives of this study were to evaluate the impact of EUFs in process of controlled-release their effect on growth of Chinese kale (*Brassica alboglabra* Bailey).

MATERIALS AND METHODS

Experimental procedures and details

Commercial urea fertilizer granules were purchased from the C.P. Trading Group Co., Ltd., Thailand. Polyvinyl alcohol (PVA) was purchased from Aldrich chemicals. Polyvinylpyrrolidone (PVP) was purchased from Acros Organics. Other chemicals and solvents were all of analytical grade. Deionized water was used throughout the experiment. Osmocote® (13-13-13) was purchased from Sotus International Co., Ltd., Thailand.

Six combinations among PVA and PVP were showed in Table 1. Appropriate amounts of the two solutions were mixed in the selected blend ratios, 1:0, 1:0.25, 1:0.5, 1:1 and 1:2 PVA/PVP by mass. A controlled experiment without any coating material was also carried out.

In the experiment, eight different materials coating of urea granules, un-coated urea and osmocote® (13-13-13) were applied at rate of N 30 kg/ha, as follows: (1) Unfertilized control; (2) un-coated urea; (3) EUF2; (4) EUF3; (5) EUF6; (6) Osmocote®; (7) PVP and (8) PVA. Plots were arranged in a completely randomized design in the greenhouse with five replicates. Before the onset of the experiment, soil samples were collected and analyzed for chemical properties.

Determination of urea

A solution (0.5 mL) containing 4% (w/v) of *p*-dimethylaminobenzaldehyde and 4% (v/v) sulfuric acid in absolute ethanol was added to 2 mL of a solution of urea. After 10 min of reaction at 25°C, the absorbance of the solution was measured at 422 nm against a reagent blank using a spectrophotometer (Spectronic 21, Milton Roy Company). The concentrations of the yellow-colored compound in the samples were determined by reference to the calibration curve (Knorst *et al*., 1997).

Investigation controlled-release behavior of EUFs

The release urea solution of EUFs in the containers was obtained and kept at 4°C to determine the content of urea by spectrophotometer method. Triplicate experiments were prepared at the same time. The release results were analyzed by using an empirical equation to estimate the value of n and K as follows (Al-Zahrani, 1999; Peng *et al*., 2006);

$$M_t/M = Kt^n \text{ or } \log(M_t/M) = \log(K) + n\log(t) \qquad (1)$$

Where M_t/M is the release fraction at time t, n is the release exponent value, and K is the release factor. From the slope and intercept of the plot of $\log(M_t/M)$ versus $\log(t)$, the kinetic parameters n and K were calculated.

Measurement of the water retention of EUF in sand

Two grams of EUF were well mixed with 200 g of dry sand and kept in a container and then 200 g of deionized water was slowly added into the container and weighed (*W1*). A controlled experiment, i.e., without EUF, was also carried out. The containers were maintained at 25°C and were weighed every 4 days (*Wi*) over a period of 28 days (Wu and Liu, 2008). The water retention ratio (*WR%*) of sand was calculated using the following equation;

$$WR\% = (W_i - W_1) \times 100 / 200 \qquad (2)$$

Observation of plant growth

The soil sample was pre-incubated at imposing place for 7 days for moisture elimination. Pot diameter was 15 x 13 cm and soil was taken in 40 pots which contained 3 kg of soil per pot. The experiment was conducted in a naturally lit greenhouse, located at the Suranaree University of

Table 1 The combinations among PVA/PVP in different ratio.

Combination	PVA	PVP
EUF 1	2	0
EUF 2	1	0
EUF 3	1	0.25
EUF 4	1	0.5
EUF 5	1	1
EUF 6	1	2

Technology, Thailand, during October–November 2012, and temperature was between 20-30°C. Chinese kale (*Brassica* species) was grown in freely draining pots containing soil. Seeds were first sown in germination pots, and 2 weeks after germination uniform seedlings were transplanted at a rate of one plant per pot.

In the experiment, eight different fertilizers were applied at 30kg N/ha. Fertilizer was added into the pot after transplanting for 7 and 14 days. All plants were well watered daily until harvesting stage. The morphological characteristics of the crop like shoot and root length and leaf area (LA) were recorded. Plant growth parameters were investigated as followed; fresh and dry weight and element analysis including nitrogen (N), phosphorus (P) and potassium (K). N was analyzed by Kjeldahl method (Abraham and Rajasekharan, 1996). P was analyzed by Vanadomolybdate Barton method (Barton, 1948). K was determined by Flame photometer (Plant analysis handbook of reference method, 1999).

Statistical analysis

All data were subjected by analysis of variance (ANOVA) and means were separated by Duncan's multiple range tests (SPSS® software for WINDOW™, Version 13.0; SPSS, Chicago, IL). Significance of differences was established at $P \leq 0.05$.

RESULTS

Controlled-release behavior of EUFs

The releasing process of coated urea in water could be described as the following process. Water penetrated through the coating shell and then dissolved urea into the water medium through the coating shell. Figure. 1A showed the cumulative released quantity versus time from PVA in different coating quantities. Coating materials were prepared with PVA solutions used as plasticizer and additive PVP solutions that can greatly improve membrane oxidative stability and chemical stability (Jinly *et al*., 2010) given in Table 1.

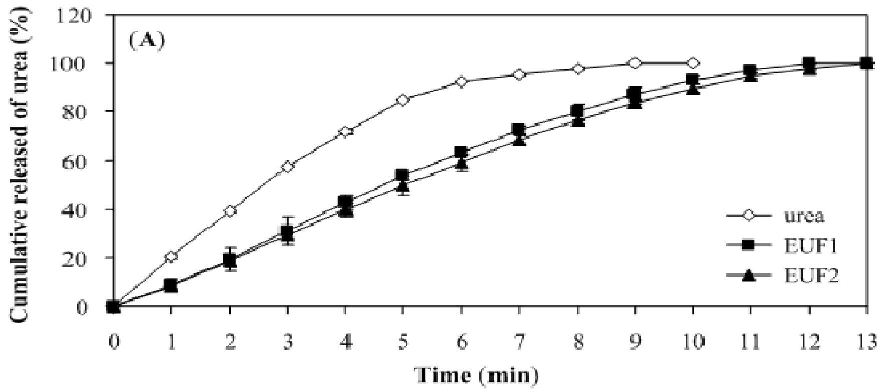
The coated urea was released at a constant rate in the first stage (initial state) and then released slowly till the end. The PVA coated urea particle (EUF1) release was 54% and 93% at 5 min and 10 min, respectively, while the EUF2 release was 50% and 90% at 5 min and 10 min, respectively. The un-coated urea release was faster for 85% at 5 min and 100% at 10 min until endpoint.

Figure. 1B showed the cumulative released quantity versus time from PVA and PVP in different ratios. The EUF3 was released 45% at 5 min and 84% at 10 min while the EUF4 was released 48% at 5 min and 90% at 10 min. The EUF5 was released 51% at 5 min and 87% at 10 min. The EUF6 was released 56% at 5 min and 94% at 10 min. Similar trends were observed for the concentration dependence, where the PVA/PVP mass ratio ranged from 1:0.25 to 1:2. It depended on the PVP content. It could clearly be seen that the trends of releasing of urea was increased when increasing PVP content. Due to the hydrophilic nature of PVP (Rakesh *et al*., 2008), the biopolymer would be released well in water.

From the plot of log (Mt/M) versus log (t), the n and K values have been calculated. The n value is an empirical parameter characterizing the release mechanism. On the basis of the diffusion exponent, an n value of 0.5 indicates the nutrient release mechanism approaches to a Fickian diffusion controlled release, whereas n equal to 1.0 indicates the nutrient release mechanism approaches to zero-order release. The n value from 0.5 to 1.0 is a nutrient release mechanism for non-Fickian diffusion. Table 2 summarized the values of urea release from EUF. The n values of all EUF were in the ranged from 0.95 to 0.98, which were higher than un-coated urea (0.70). It could be concluded that the high n value refers to the longer nutrient release that benefits plant absorption.

Water retention of EUFs in sand

The most of important application of EUFs is for agriculture and horticulture, especially for saving water in dry or desert regions. The slow solubility of granular fertilizer can be helping regularly absorption of nutrients for plants growth. Therefore, it is necessary to investigate the water-retention ability of EUFs in sand.



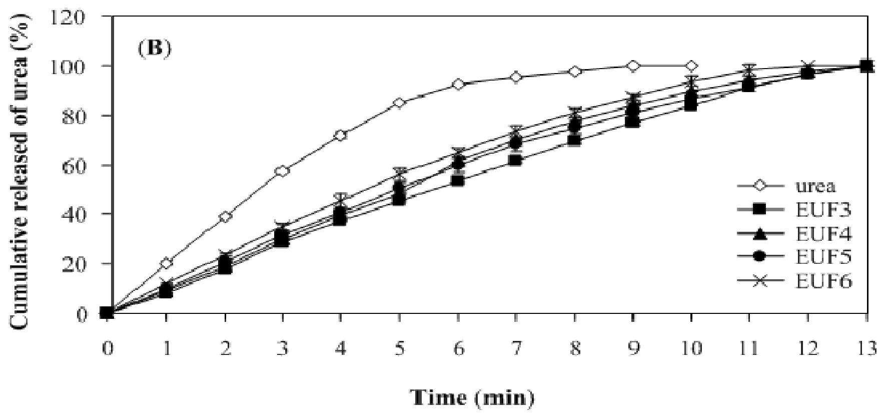


Figure 1. Cumulative released quantity of urea and urea coated versus time, (A) release behaviors of urea, EUF1 and EUF2 for PVA; (B) release behaviors of urea, EUF3, EUF4, EUF5 and EUF6 for PVA and PVP.

Table 2 The release factors (*K*), release exponents (*n*), and determination coefficients (r^2) following linear regression of release data of urea from EUF.

Sample	*n*	*K*	r^2
urea	0.70	23.97	0.9468
EUF1	0.95	10.44	0.9827
EUF2	0.98	9.37	0.9867
EUF3	0.96	9.14	0.9910
EUF4	0.93	10.22	0.9832
EUF5	0.88	11.24	0.9858
EUF6	0.86	13.05	0.9922

The water retention ratio of sand without EUFs (Figure. 2A) showed lower retention values. After 21 days, the value was almost zero, consequently the water was completely evaporated. Figure. 2B showed the water retention ratio of sand with EUFs was strongly reserved water. Similar trends were observed for the concentration dependence, where the PVA/PVP mass ratio ranged from 1:0.25 to 1:2.

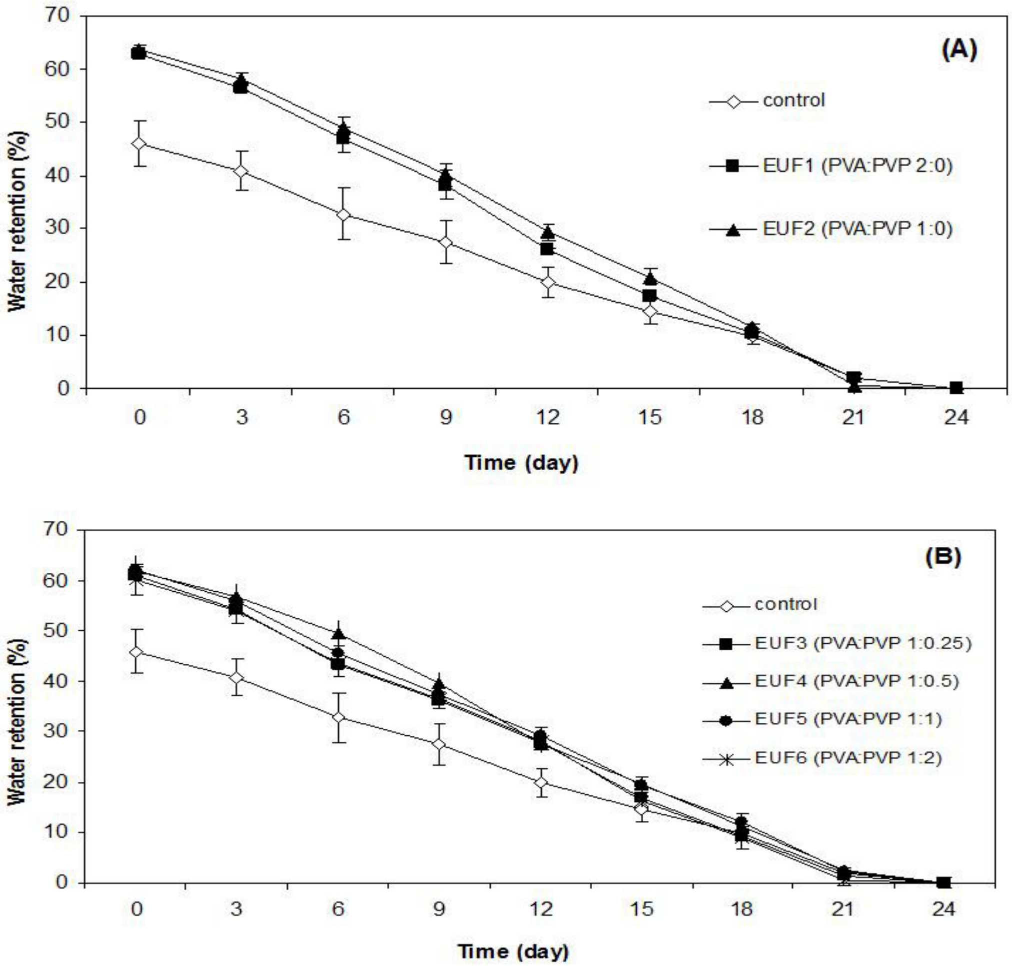


Figure 2. (A) Water-retention behavior of sand with two formula EUFs (EUF1 and EUF2) and sand without EUF as control; (B) Water-retention behavior of sand with four formula EUFs (EUF3, EUF4, EUF5 and EUF6) and sand without EUF.

Plant analysis

A soil test was taken from each plot before sowing. Soil was planted with pH 7.75, organic matter content 7.4 % and adequate level of available P and K. N levels (0.37 mg/kg) was not a serious concern because observing urea could be truly affected on plant (Table 3).

From the data of plant growth found that urea coated with biopolymer can be stimulated plant growth higher than control. Chinese kale planted with EUF2 and EUF3 had significantly ($P \leq 0.05$) increased the fresh weight and dry weight compared to plants with urea and control (Table 4). Stem length showed a significant different at P value ≤ 0.05 highest in urea, EUF2, EUF3 and EUF6. Root length showed significantly highest in EUF2 treatment. Plants with control, osmocote, PVP and PVA resulted in low of stem and root dry weight (Table 5). These suggested that PVA or PVP did not available to Chinese kale plants for growth and development. Application of coated urea was slightly increased leaf area, while control, osmocote, PVA, and PVP was slightly smaller leaf area.

The percentage of total N in leaves of kale was determined by Kjedahl method. Also showed total N accumulation ranged from 3.49-5.24% (Table 6). Chuphutsa (2010) showed content of total N in kale (*Brassica oleracea*) ranged from 3.00-5.18%.

The level of mineral N in soil before and after fertilizer application is index which determines lost of N from the level of N absorbed by plants. The content of N loss was ranged from 10.61-17.19 mg/kg (Figure. 3). This investigation showed that coated urea was lower N loss than un-coated urea. Application of coated urea was improved effect on plant with the optimum N applied via CRFs was due mainly to their positive action on growth. Under the experiment, the calculation of the N budget inputs 30 kg N/ha for testing N loss found that urea coated

Table 3. Chemical characteristics of the soil before fertilizer applications.

Parameter	Value
pH (water, 1:1)	7.75
OM (%)	7.4
EC (mS/cm)	0.33
Available N (mg/kg)	0.37
Available P (mg/kg)	29.6
Available K (mg/kg)	877.15

Table 4. Fresh weight, dry matter weight, in stem and root of kale which treated with un-coated urea, coated urea, Osmocote, PVA, PVP and without fertilizer as control.

Treatment	Fresh weight (g/plants)		Dry weight (g/plants)	
	Stem	Root	Stem	Root
Control	3.95^{c}	0.36^{d}	0.41^{c}	0.07^{c}
Urea	36.05^{b}	1.82^{bc}	3.64^{b}	0.37^{b}
EUF2	44.18^{a}	2.86^{a}	4.56^{a}	0.56^{a}
EUF3	43.84^{a}	2.33^{b}	4.64^{a}	0.52^{a}
EUF6	39.95^{ab}	1.77^{c}	4.32^{a}	0.42^{b}
Osmocote	6.26^{c}	0.26^{d}	0.55^{c}	0.05^{c}
PVP	3.42^{c}	0.18^{d}	0.35^{c}	0.03^{c}
PVA	2.15^{c}	0.16^{d}	0.26^{c}	0.04^{c}
% CV	11.54	24.17	12.75	21.06

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

Table 5 Stem length, root length and leaf area of kale which treated with un-coated urea, coated urea, Osmocote, PVA, PVP and without fertilizer as control.

Treatment	Stem length (cm)	Root length (cm)	Leaf area (cm^2)
Control	20.50^{cd}	9.83^{bc}	74.53^{cd}
Urea	39.67^{a}	15.67^{ab}	455.47^{b}
EUF2	37.33^{a}	22.33^{a}	569.15^{a}
EUF3	33.16^{b}	16.00^{ab}	542.77^{a}
EUF6	37.33^{a}	15.67^{ab}	468.45^{b}
Osmocote	21.83^{c}	12.5^{bc}	109.96^{c}
PVP	18.00^{d}	7.33^{c}	61.19^{cd}
PVA	14.66^{e}	12.00^{bc}	39.83^{d}
% CV	6.69	30.36	12.44

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

Table 6 Element analysis of Kale in the values of nitrogen (%N) by Kjedahl method and total N/plant (from dry matter) which treated with un-coated urea, coated urea, Osmocote, PVA, PVP and without fertilizer as control.

Treatment	% N	Total N/plants
Control	4.05^{b}	1.68^{d}
Urea	4.04^{b}	13.29^{c}
EUF2	5.24^{a}	24.14^{a}
EUF3	5.12^{a}	24.56^{a}
EUF6	3.62^{c}	16.63^{b}
Osmocote	3.56^{c}	2.16^{d}
PVP	3.49^{c}	1.36^{d}
PVA	3.63^{c}	1.05^{d}
%CV	3.53	7.08

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

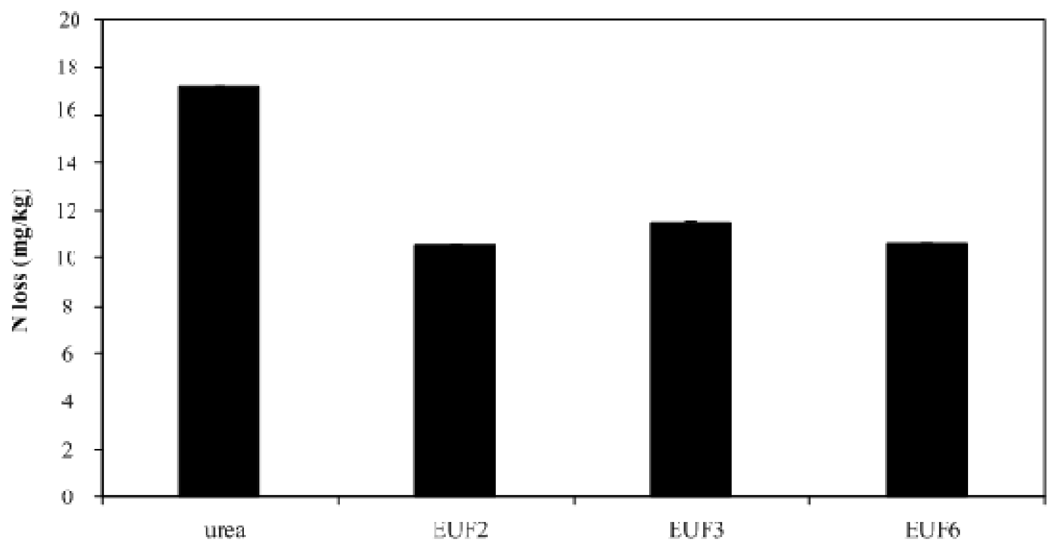


Figure 3. N loss (mg/kg) in soil treatments of coated urea in various formula (EUF2, EUF3 and EUF6) and un-coated urea.

with PVA and PVP showed lower N loss when compared with un-coated urea, thus resulting in this work.

Under normal soil conditions, NH_4^+ are absorbed by the soil become attached to the negatively charged soil particle. N becomes available to plant, either in its NH_4^+ form or as nitrate (NO_3^-) following microbial oxidation. In the experiment, a soil test was taken from each of 40 plots after kale plant culture had showed in Table 7. The data was showed a decreasing nutrient which compared with original soil. The levels of N started at 0.37 mg/kg and decreased between 0.20-0.33 mg/kg. The levels of organic matter (OM) started at 7.4% and decreased between 4.03-6.56%. The high levels of percentage OM showed in coated urea (EUF2, EUF3, and EUF6). The lower value of percentage OM showed in control, osmocote, PVP, and PVA.

The levels of available P started 29.6 mg/kg and decreased between 11.46-28.12 mg/kg. The levels of available K started 877.15 mg/kg and decreased between 715.41-818.69 mg/kg. Moisture content played an

Table 7 Chemical characteristics of the soil after kale plant cultivation.

Treatment	pH	EC (mS/cm)	moisture	% OM	N (mg/kg)	P (mg/kg)	K (mg/kg)
Control	7.78	0.33	27.1	4.03[f]	0.20[f]	11.46[g]	818.69[a]
Urea	7.87	0.31	22.2	5.83[bc]	0.29[bc]	28.12[a]	715.41[d]
EUF2	7.84	0.33	10.4	6.56[a]	0.33[a]	22.55[b]	733.73[cd]
EUF3	7.84	0.31	22.7	6.42[ab]	0.32[ab]	19.09[de]	730.31[cd]
EUF6	7.82	0.33	32.3	6.38[ab]	0.32[ab]	14.09[fg]	761.01[bc]
Osmocote	7.85	0.33	27.8	4.31[ef]	0.22[ef]	20.12[cd]	812.93[a]
PVP	7.83	0.35	24.3	4.73[de]	0.24[de]	24.70[b]	793.22[b]
PVA	7.77	0.36	26.1	5.31[cd]	0.27[cd]	16.31[ef]	769.54[b]
%CV	-	-	-	5.38	5.38	6.67	1.89

Values followed by the same letter are not significantly different at P ≤ 0.05 by DMRT

Figure 4. Kale plant harvesting stage treat with (a) control; (b) urea; (c) EUF2; (d) EUF3; (e) EUF6; (f) Osmocote; (g) PVP and (h) PVA.

important role in determining soil resistance to penetration and as the soil moisture increased, the resistance decreased for this treatment. This decrease in soil resistance did not differ between treatments except EUF2.

Data in this results showed that N influenced on growth that marketable on weight of kale, which indicated the efficiency of fertilizer on product of plant. From this work would summarized the quality of coated urea was enhanced the growing of kale under greenhouse cultivation. It is obvious that in dry weight, length of stem, and leaf area index of kale, including physiological are well characteristics (Figure. 4).

DISCUSSION

The reduction in urea release of granules with a smaller quantity of PVA was obvious. Probably, PVA increased the hydrophobic and thereby reduced the water-sensitivity of the PVA coating (Pemberton and Jaeger, 1996). Therefore, the uptake of water and as a result the release of urea was decreased. Besides the hydrophobicity, also the coating quality had a major influence on the release of urea.

EUFs that were maintained water retention in sand. It was indicated that all EUF had good water-retention capacity. That could be saved and managed water. Furthermore, the quality of EUFs inputs affects on plant growth. We saw a significant increase in plant biomass. According to Wilson *et al*. (2006), fertilizer management is an important aspect of growing high yielding in brassica crops.

The key drivers of soil fertility for crop production in general are N and P (Moot *et al*., 2007). For inorganic fertilizers (urea) are usually high soluble and are more rapidly available for plant growth. Some inorganic fertilizers (EUF2, EUF3, and EUF6) were coated with biopolymers to slow down the release of nutrients. Leaf area is important in determining yield through radiation interception (Monteith, 1977) and biomass production (Watson, 1958; Nanda *et al*., 1995).

The coated urea have reduced NH_3 volatilization and encouraged more efficiency utilization than un-coated urea. Because of high release N is effected on rapid urea hydrolysis which increased greater potential for NH_3 lost under alkaline soil condition (soil pH). In fact, when preferred N sources are available for plant, the utilization of the alternative N sources and most organic molecules is repressed. This mechanism is known as N regulation (Magasanik, 1993). Following the interaction of N mineralization and immobilization processes is closely tied to the carbon cycle, because decomposing microorganisms derive their energy from carbon compounds they find OM in soil. Activity of soil microbes is mainly stimulated by NH_4^+. Immobilized N it is not immediately available for plant uptake, but need to be mineralized first. It is also one cause that OM was decreased due to decompose by microorganism.

From this work would summarized the quality of coated urea was enhanced the growing of kale under greenhouse cultivation. EUFs have to be considered recommendations in order to minimize use of N fertilizers. Application of coated urea was improved effect on plant with the optimum N applied via EUFs was due mainly to their positive action on growth.

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