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DEVELOPMENT OF SLOW RELEASE ORGANIC FERTILIZER WITH SUPERABSORBENT AND MOISTURE PRESERVATION PROPERTIES FROM SUGARCANE BAGASSE

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ABSTRACT

Efficient assimilation of nutrients in farm lands and improvement of soil water retention capabilities can be achieved through the application of controlled release fertilizers. The ideal fertilizer should be able to provide essential nutrients and preferably with reasonable water holding capacity, be environment friendly and affordable. In addition, utilization of raw materials available in nature and their application to derive other useful products without any adverse impact on the environment has long been a desired goal. A controlled release organic fertilizer with superabsorbent and moisture preservation properties was prepared from sugarcane bagasse (SCB), a lignocellulosic waste of sugarcane industry, as the source of the organic material and *N,N'*-methylene-bis-acrylamide (NNMBA) as crosslinker. The influence of SCB, crosslinker, reaction time, reaction temperature and acrylic acid neutralization on water absorbency was investigated. Macro and micro nutrient properties of the fertilizer and SCB were studied using Kjeldahl, flame photometry, Olsen method (colorimetry) and AAS, while characterization was done using FTIR. The nutrient release and moisture retention behaviour of the fertilizer treated, and untreated soil were also investigated. Water absorbency of fertilizer and SCB was found to be 2.12 g and 0.53g per gram sample respectively, when allowed to swell in tap water for one hour at room temperature. The results of nutrient analysis showed that the fertilizer contained 2.06% N, 2.51 ppm P and 9.94 ppm K while SCB contained 0.88% N, 0.91 ppm P and 5.42 ppm K. Although similar properties of the fertilizer were found in raw SCB, experimental results revealed that the fertilizer product possessed superior properties such as controlled release, superabsorbent and moisture preservation capabilities, which justified that it could be used as a bio-fertilizer for agricultural and horticultural applications, especially in areas that experience low rainfall patterns.

Key words: Fertilizer, control release, sugarcane bagasse.

INTRODUCTION

Decline in soil fertility and high cost of fertilizers are key factors limiting agricultural production in many developing countries (Nakhone and Tababa, 2008). Fertilizers and water have been known to be the main factors that limit the production of agriculture (Liu *et al.*, 2006). It is therefore fundamental to try to improve the efficient utilization of fertilizer nutrients and water resources in crops for sustainable agricultural production (Guo *et al.*, 2005). Fertilizers are responsible for substantial increases in crop yields and allow crops to be planted in soil that would otherwise be nutrient deficient (Freeman and Omiti, 2003). The relative significance of fertilizers is increasing as the population grows and as more developing countries increase their fertilization rates (Müller and Niemsdorff, 2006). This calls for alternative cheaper sources of fertilizers, especially from agro-industrial wastes, in attempts to reduce high costs of farm inputs as well as running costs of the same industries (Jama and Pizarro, 2008; Wallace and Knausenberger, 1997).

Little assimilability of most mineral fertilizer's micronutrient components has been a cause for serious environmental concern. About half of the applied fertilizers are lost to the environment either through run off, leaching or evaporation, and cause ground water contamination (Bhattacharya *et al.*, 2007). Such wastes are also a major economic draw back (Guo *et al.*, 2006). In the light of the above facts, it is important to increase the effectiveness of plants' nutrient absorption and to decrease losses, while at the same time limit the amount of fertilizers' waste material produced by the industry through development of cost effective slow release fertilizers (Lubkowski and Grzmil, 2007; Talaat *et al.*, 2008).

Slow release fertilizers (SRFs) are designed to release nutrients slowly, at rates that coincide with nutrient requirement of the plant (Liang *et al.*, 2007). They belong to two categories depending on the mechanism of nutrient release. In the first category, nutrients release to plants is governed by either hydrolysis or diffusion or they may be present in forms that are extractable by plant roots. Membrane coated urea formaldehyde fall into this group

(Rahman *et al.*, 2008; Guo *et al.*, 2006; Desmond *et al.*, 1997). In the second category, nutrients are present in exchangeable or chelate-extractable positions, and fertilizers in this group mimic natural forms of soil nutrients. Synthetic ion exchange resin based fertilizers as well as polymer based compounds fall into this category (Bhattacharya *et al.*, 2007; Dailey, 2006; Joergensen, 2006). SRFs minimize leaching and the frequency with which plants must be fertilized (King *et al.*, 2005). These fertilizers have been reported to supply adequate nutrition for 3 to 12 months (Conover and Poole, 1981).

Plant derived by-products have enormous potential to inspire and influence modern agrochemical research (Khanam *et al.*, 2006; Benner, 1993). Sugarcane bagasse (SCB) is a good example of agro-industrial waste (Costa *et al.*, 2005). About 54 million dry tons of SCB is produced annually throughout the world (Mulinari *et al.*, 2009; Sun *et al.*, 2003). It is used either as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products, various types of building boards, and certain chemicals. However, these represent only a small fraction of the total bagasse produced. These agro-industrial residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass, particularly for the production of oil sorption- active materials and organic fertilizers (Rabelo *et al.*, 2008).

The ever-increasing population is faced with decreasing food production, due to high costs associated with farming among other factors. Most of the commercially available fertilizers have negative effects on the environment due to their high leachability and solubility. An application of the SRFs, which release their nutrients according to plant requirements, ensures an improved effectiveness of fertilizing through minimizing the losses between application and absorption. They were first used in 1965. Currently, the SRFs are produced mainly in the USA, Western Europe, Japan, South Korea, Israel and China (Lubkowski and Grzmil, 2007).

EXPERIMENTAL MATERIALS

Acrylic acid, carboxymethyl cellulose sodium salt, epichlorohydrin, cyclohexane (dispersion medium), *N, N*-methylene-bis-acrylamide and potassium persulphate were of analytical grade purchased from Kobian Kenya Limited. Span60/Sorbitan monostereate of analytical grade was supplied by Fisher Scientific East Africa Kenya limited. All other materials used were of analytical grade and were used directly as received. Fresh SCB was obtained from Nzoia Sugar Company, dried under green house and ground into powder. To confirm results and minimize errors, all the preceding tests were replicated and the average values taken as the result.

Experimental procedure

The development of a slow release organic fertilizer with superabsorbent and moisture preservation properties (SROFSMP) was done according to the procedures developed by Wu *et al.*, (2008), Mo *et al.*, (2006), Liang *et al.*, (2007), Liu *et al.*, (2007) and Guo *et al.*, (2005). Samples were prepared using varying amounts of SCB, NNMBBA, different degree of acrylic acid neutralization by ammonia and under different reaction temperatures. These reactions were conducted in a three-neck round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. 10 g of SCB was added into the flask after being comminuted into powder. This was followed by addition of 10 g carboxyl methyl cellulose sodium salt and 60 mL of cyclohexane (dispersion medium). The mixture was stirred for 30 min at room temperature, after which 8 g of the crosslinker (*N, N*-methylene bisacrylamide) was added into the flask. The mixture was then heated to 40 °C with vigorous stirring for 1 h. The crude product formed was cooled, filtered to remove cyclohexane and then oven dried at 60 °C. 5g sample of dry granules was added into a flask.

2 g of potassium persulphate and 20 mL solution of acrylic acid (partly neutralized by 2 mL ammonia) were transferred into the flask after soaking for 30 min. 60 mL of cyclohexane and 3 g span-60 were also added into the flask and stirred continuously for 2 h at 60 °C. After the reaction was completed, the suspension solution was filtered and the product oven dried at 40 °C to obtain the

desired brown granular fertilizer product (SROFSMP).

Characterization of the fertilizer and bagasse by FTIR

Development of a new slow-release superabsorbent fertilizer involves formulation, characterization, and testing. The components of the fertilizer were analyzed using a Fourier-transform infrared (FTIR) spectrophotometer (American Nicolette Corporation, Model 170-SX). As a control, untreated SCB was also characterized. The dry samples were ground with dried KBr powder. The KBr disks were subjected to the FTIR spectrophotometry.

Measurement of water absorbency of the fertilizer and sugarcane bagasse

1 g of accurately weighted fertilizer samples were immersed into 100 mL of tap water and allowed to soak at room temperature for 1 h to reach swelling equilibrium. The swollen samples were separated from non absorbed water by filtering through filter paper under gravity for 30 minutes and weighed. The water absorbency (QH₂O) of the fertilizer was determined by weighing the swollen samples and QH₂O calculated using Equation 1.

$$QH_2O = \frac{M_2 - M_1}{M_1} \quad (1)$$

Where M_2 and M_1 referred to the weight of water swollen and dry samples respectively. The QH₂O value was expressed as the grams of absorbed water per gram of dried sample.

Measurement of time dependence of QH₂O

The time taken by fertilizer to reach swelling equilibrium in different solutions was determined. Untreated SCB was also tested as a control. 1 g of dry samples were accurately weighed, added into identical 100 mL beakers and filled with distilled water (100 mL), tap water (100 mL) and 0.9 % NaCl solution (100 mL) respectively. The swollen samples were filtered through a sieve to remove non-absorbed water and weighed. Separately, identical samples incubated were weighed at 10, 20, 30, 40, 50, and 60 min after the addition of respective samples. QH₂O was then calculated using Equation 1.

Slow release behaviour of fertilizer sample in water

To study the slow release behaviour of fertilizer and SCB samples in soil, 1 g of respective sample was thoroughly mixed with 50 g dry soil and kept in a 100 mL beaker. The beakers were covered using aluminium foil and incubated for different periods of time at room temperature. The soil was maintained at 40 % water-holding capacity by periodically weighing and adding distilled water when necessary throughout the experiment. Untreated blank control experiments were also carried out. After incubation periods of 1, 2, 5, 10, 15, 20, 25 and 30 days at room temperature, samples were oven dried at 40 °C and estimated for the nutrient contents. The nitrogen content was determined using the Kjeldahl method. Potassium was determined using flame photometer (Jenway pfp7 model) and phosphorus via the Olsen method (colorimetry) according to Okalebo *et al* (2002).

Measurement of water infiltration ratio of soil

The largest water holding ratio of soil containing fertilizer and SCB was investigated. 2 g of the fertilizer was accurately weighed, mixed thoroughly with 100 g dry soil and placed in a packing column of 4 cm diameter. The bottom of the tube was sealed by cotton wool and weighed (W_1). The soil samples were slowly drenched by tap water from the top of the tube until the water seeped out from the bottom. The weight of the column was again recorded (W_2) without seeping water at the bottom. A control experiment without sample was also carried out. The largest water-holding ratio (% Wt) of the soil was calculated using Equation 2.

$$\%Wt = \frac{W_2 - W_1}{W_2 - W_1 + 200} \times 100 \quad (2)$$

Measurement of the water retention of sample in soil

To evaluate the water evaporation rate of fertilizer and SCB treated soil, the following experiments were carried out: Typically, 100 g of dry soil was thoroughly mixed with 2 g fertilizer sample and placed in beaker **a**.

Another 100 g of dry soil without sample was placed in an identical beaker **b**. 200 mL of tap water was slowly added into both beakers. The beakers were kept under identical conditions at room temperature for 30 days. The initial masses of the mixture (W_i) in the two beakers were measured after removal of excess water and their masses recorded every 5 days (W_f) to compare the water retention of the sample. The same was repeated for SCB sample and the water-retention (% WR) calculated using Equation 3.

$$\%WR = \frac{(W_i - W_f) \times 100}{100} \quad (3)$$

Determination of N P K component of fertilizer and bagasse

The amount of nitrogen in the fertilizer and bagasse samples were determined using the Kjeldahl method of distillation. The percentage nitrogen in the samples was calculated using Equation 4.

$$\%N = \frac{(T - B) \times N \times 1.401}{g \text{ sample}} \quad (4)$$

Where T= ml of sample titrated; B= ml of blank titrated; N= acid normality

Fertilizer and bagasse samples were analyzed for phosphorus using the Olsen method. The concentration of P in samples was expressed in P mg kg⁻¹ using Equation 5.

$$P(\text{mg kg}^{-1}) = \frac{(a - b) \times v \times f \times 1000}{1000 \times w} \quad (5)$$

Where a= concentration of P in sample; b= concentration of P in blank; v= volume of extracting solution; f= dilution factor; w= weight of sample

Flame photometric method was used to determine the potassium content of the fertilizer and bagasse samples. The concentration of K in samples was expressed in K mg kg⁻¹ using Equation 6.

$$K(\text{mg kg}^{-1}) = \frac{(a - b) \times v \times f \times 100}{1000 \times w \times 1000} \quad (6)$$

Where a= conc. of K in digest; b= conc. of blank digest; w= weight of sample; v= volume of digest solution; f= dilution factor

Determination of Cu, Fe and Zn component of fertilizer and bagasse using AAS

For micronutrients determination in soil and bagasse samples, samples were first digested in a mixture of sulfuric acid, salicylic acid, hydrogen peroxide and selenium powder. Standard solutions for respective cations were made. Digested samples were then wetted with small amounts of deionized water and brought into solution using 2 mL conc. HCl, then diluted to 100 mL final volume with distilled water. The final volume was based upon predicted concentrations of each element to ensure that the resulting actual concentrations were not below the detection limits. For the AAS detection of Zn, Cu, and Fe, aliquots of the above HCl solution were diluted using 1 mL of unknown plus 9 mL of respective standards.

RESULTS AND DISCUSSION

Chemical analysis of the SROFSMP and SCB

The fertilizer contains essential macro and micro nutritional values needed for agricultural soil and plant growth. One of the particularities of the fertilizer is the ability to absorb moisture in substantial quantity and pass the moisture to the soil at a considerable period of time. The fertilizer also gives the soil a granular structure, eliminating negative effects such as soil hardening that is associated with conventional fertilizers. Table 1 summarizes the chemical composition of the developed SROFSMP and control sample (untreated SCB) used as starting material for the SROFSMP development. The N component (2.01%), P (2.51 ppm) and K (9.94 ppm) in the SROFSMP are key nutrients necessary for plant growth. The fairly neutral pH level of the SROFSMP is desirable for nutrient uptake by plants and can serve to reduce soil acidity, which is characteristic of many Kenyan farm lands. Macro and micronutrient levels in the untreated SCB differ from that of the SROFSMP. The water absorbency of the SROFSMP is four fold that of the control sample.

Table 1: Summary of the SROFSMP and the control (SCB) composition

Component	SROFSMP	Control
Nitrogen Content	2.06 %	0.88 %
Phosphorus Content	2.51 ppm	0.91 ppm
Potassium Content	9.94 ppm	5.42 ppm
pH	7.7	5.6
Water absorbency	2.12 g	0.53 g

FTIR characterization

Fertilizer IR (KBr disk) ν cm^{-1} : 3419 (N–H, O–H stretching), 3309 (broad O–H), 3070 (NH_4^+), 2300–3700 (broad, COOH), 2931, 1643, 1543, 1288, 1064, 687, 563. SCB IR (KBr disk) ν cm^{-1} : 3100–3600 (broad, OH), 2916 (polysaccharide C–H), 1728, 1636, 1326, 1157, 902, 833. FTIR analysis of SROFSMP (Figure 1) revealed characteristic absorption

bands at 3419 for the N–H stretch, a broad stretch between 3200–3700 for O–H, 2931 (C–H stretch and C–N of acrylate). A broad band between 2500–3800 revealed a carboxylic stretch. The presence of carboxylic acid group is further confirmed by the carbonyl stretch at 1643. The peak at 1543 corresponds to amide stretch. Infrared spectrum of SCB (Figure 2) revealed characteristic absorption peaks

between 3100-3600 for the O—H stretch and

2916 for the polysaccharide C—H.

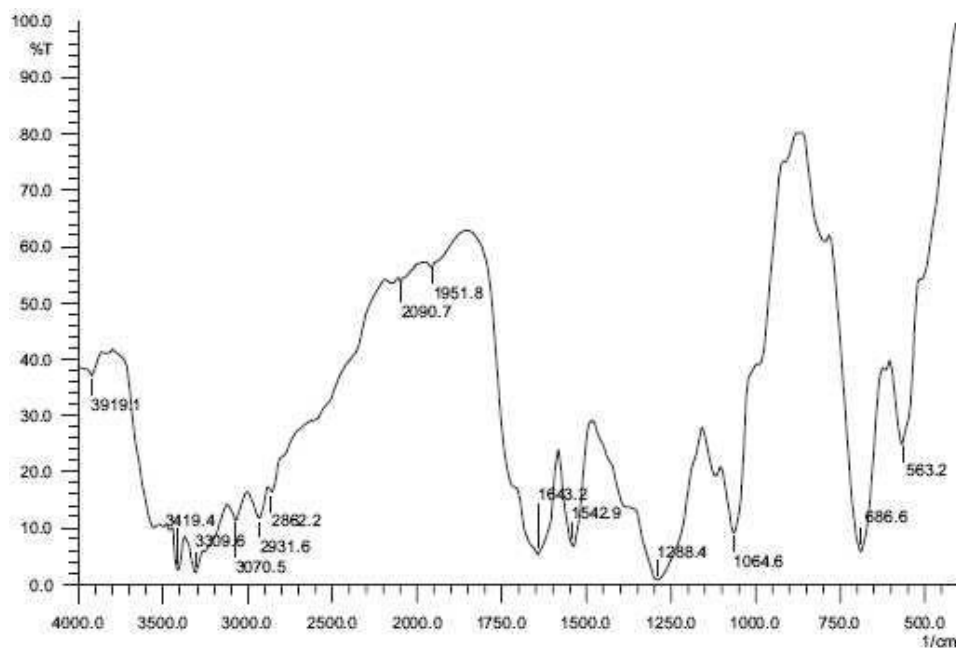


Figure 1: FTIR spectrum of SROFSMP

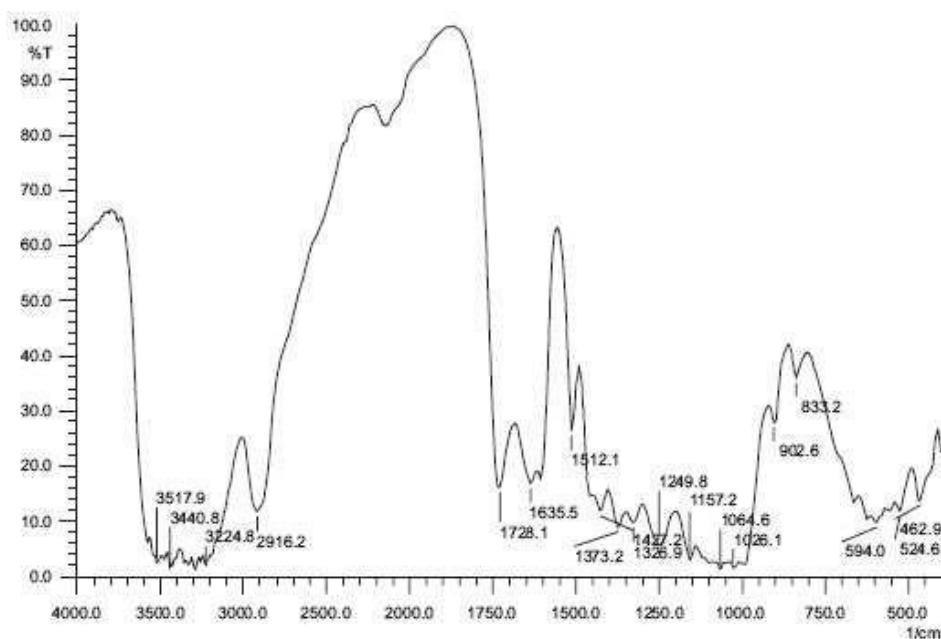


Figure 2: FTIR spectrum of SCB

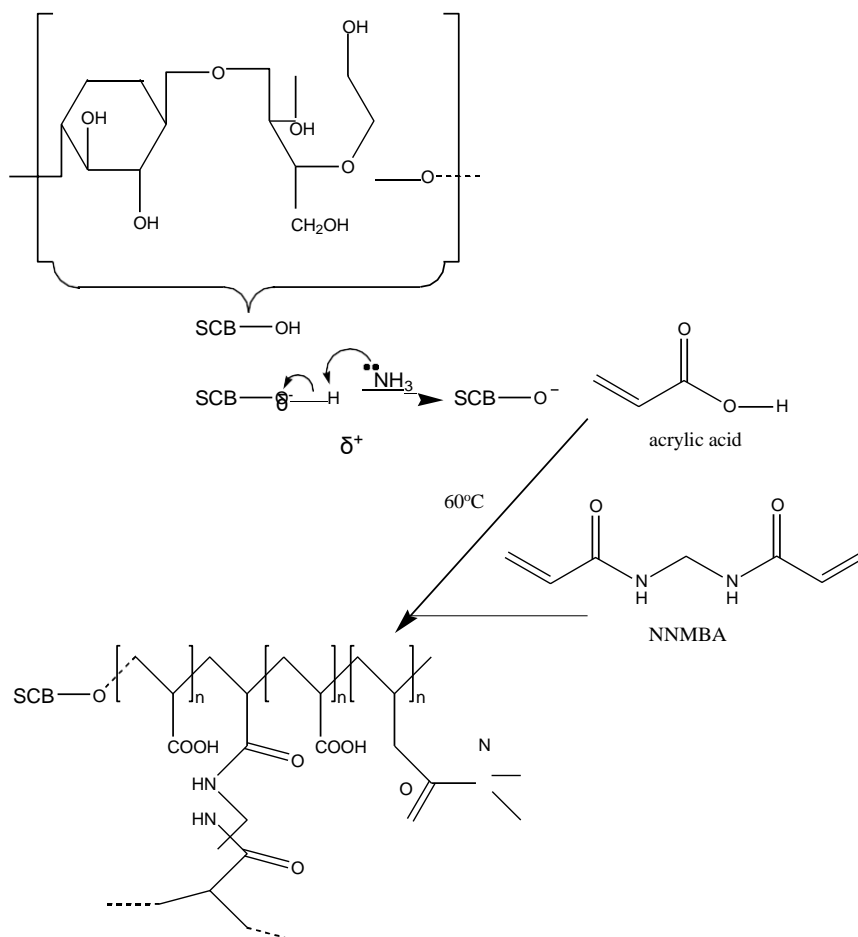
SROFSMP development and cross linking process

The proposed mechanism for cross-linking copolymerization of acrylic acid onto hydroxyl

groups of SCB is shown in Scheme 1. Ammonia abstracts a hydrogen atom from the hydroxyl groups of sugarcane bagasse (SCB—OH) to form corresponding alkoxy anions on the hydrogel. The resulting active centres then

initiates chain growth of acrylic acid and in the presence of NNMBA, crosslinking reactions occurs leading to the formation of a three

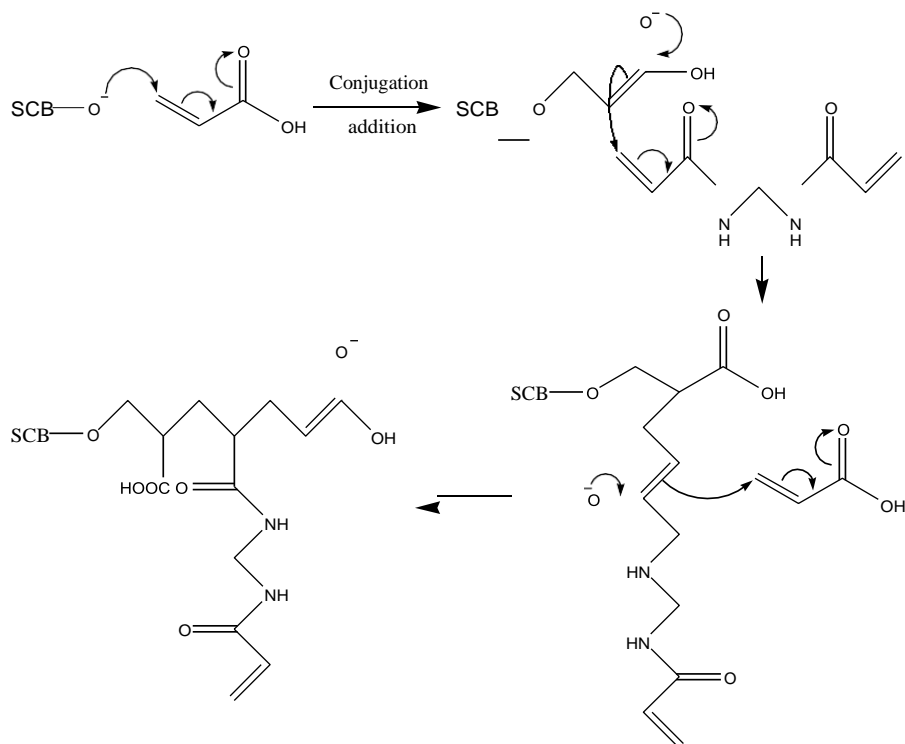
dimensional network (SROFSMP shown in Figure 3).



Scheme 1: Proposed mechanism for SROFSMP development.

Initially, the reaction undergoes Michael addition followed by successive additions to form the three dimensional network (Scheme 2). In this mechanism, the anion from SCB adds to acrylic acid in a Michael reaction to

form the enolate ion which undergoes a second conjugate addition reaction with NNMBA. The resultant enolate undergoes subsequent conjugate additions to form the three dimensional network.



Scheme 2: Proposed cross linking mechanism



Figure 3: Photograph showing SROFSMP development from SCB

Influence of reaction parameters on water absorbency

The water absorbency of a superabsorbent polymer depends on the strength of the cross-linking density, hydrophilic groups, polymer network behaviour and elasticity of the polymer networks, type of solvent and ionic

strength of the external solution. For the enhancement of water absorbency and holding capability of the product, the influences of the reaction parameters on water absorbency in distilled water, tap water and 0.9 % NaCl, such as reaction time, temperature, degree of neutralization of acrylic acid, SCB and cross

linker were studied to establish optimum amounts of these parameters for fertilizer development. Each of the experiment was replicated to confirm results and minimize errors.

Influence of reaction time

The swelling equilibrium for SROFSMP and SCB samples in different solutions was studied as a function of reaction time. It was observed that water absorbency of SROFSMP

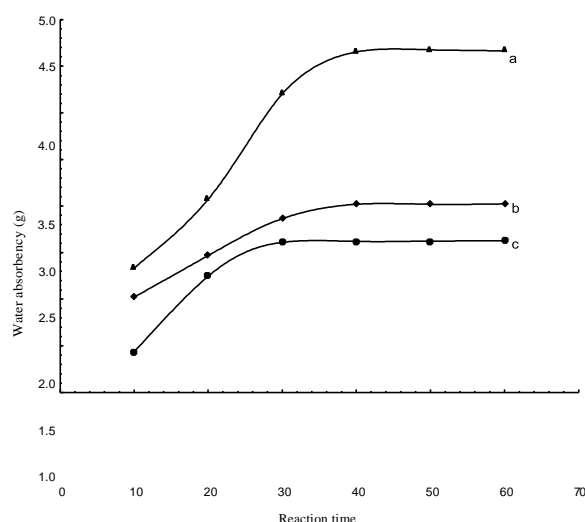


Figure 4: Reaction time influence on SROFSMP QH₂O: (a) distilled H₂O; (b) 0.9% NaCl; (c) tap H₂O.

Typically, water absorption curves show weight gain as a function of exposure time to water at room temperature. The SROFSMP and SCB reaction time curves showed hyperbolic and sigmoidal shapes respectively. In the two cases, the water absorption process increased gradually at the beginning and leveled off at some length of time where it approaches equilibrium. It is believed that the change of weight gain for both samples is a typical Fickian diffusion behaviour. This is also because monomer ratio conversion for both samples increased as reaction time increased, leading to decrease in soluble part of the fertilizer and SCB, and that reaction was completed by this time. The results also show that different solutions had little influence on the time required to reach swelling equilibrium. However, the observed swelling values in salty and tap water are lower than values measured for distilled water. This phenomenon could be attributed to charge screening effect of the salt

sample reached swelling equilibrium at 40 min in distilled water and 0.9 % NaCl, and 30 min in tap water (Figure 4). Figure 5 shows that water absorbency of SCB sample reached swelling equilibrium at 40 min, 45 min and 30 min in distilled water, 0.9 % NaCl and tap water, respectively. After 30 min, SCB water absorbency value in salty water equaled that of tap water of 0.86 g. These solutions also gave almost similar values after swelling equilibrium.

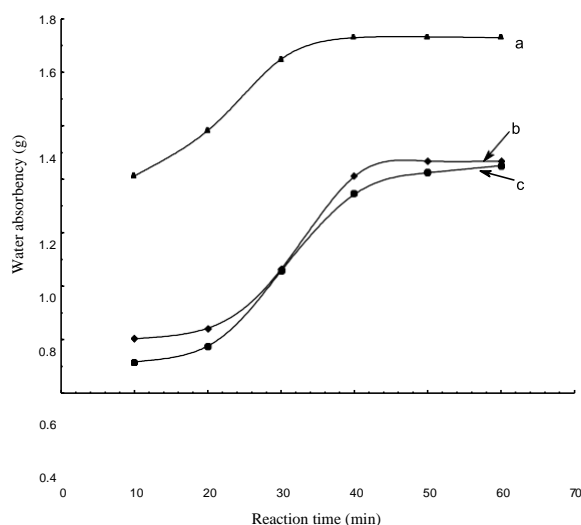


Figure 5: Reaction time influence on SCB QH₂O: (a) distilled H₂O; (b) 0.9% NaCl; (c) tap H₂O.

cations that shields the polymer hydroxyl groups, as well as ionic cross linking of salt cations with the polymer hydroxyl anions, reducing the hydrophilic capabilities of the polymer network. This effect similarly leads to decrease in osmotic pressure, a limiting factor for water absorbency, between external and internal solutions of the hydrogel network. In distilled water, absence of interfering ions was the major cause for the observed high QH₂O values. Although the fertilizer and SCB show similarity in water absorbency patterns, values observed for the SROFSMP are higher compared to values observed in the SCB sample in the three solutions. Generally, water absorption process followed the prediction of Fick's law, where concentration gradient is the driving force for diffusion (D, given in equation 7) and the amount of component diffused is a function of time as reported by Vilay *et al.*, (2008). According to this prediction, water absorbency increases with

increase in square root of time, until it reaches swelling equilibrium.

$$D = \pi \left[\frac{h}{4M_m} \right]^2 \left[\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right]^2 \quad (7)$$

Where M_m is the maximum moisture content, h is the thickness of the sample, t_1 and t_2 are the selected points in the initial linear portion and M_2 and M_1 are the respective moisture content.

Influence of SCB on SROFSMP water absorbency

The effect of the amount of SCB on water absorbency of the fertilizer was studied by varying the amount of SCB, while the amounts of other variables were kept constant throughout the experiments. SCB greatly influences water absorbency, as well as the crosslinking polymerization reactions due to the presence of porous, cellular lignocellulosic material. SCB usually posses the property of ready exchange of water, where the hydroxyl groups form the most abundant and most reactive sites on the cell wall polymers of the lignocellulosic material. Figure 6a, b and c shows water absorbency of the

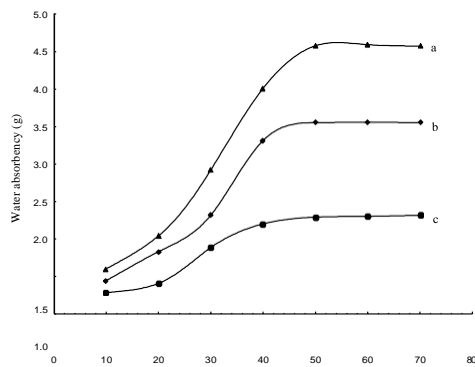


Figure 6: SCB influence on SROFSMP QH₂O (g): (a) distilled H₂O; (b) 0.9 %NaCl; (c) tap H₂O

Influence of NNMBBA

Cross linking density in polymer network is an important parameter that controls water absorbency. Significant changes in the amount of crosslinker plays a critical role in superabsorbent property modifications. This is due to the fact that crosslinker content affects crosslinking density of the hydrogel network in

fertilizer in distilled water, 0.9 % NaCl and tap water, respectively. Absorbency increased as the amount of SCB increased due to increase in the number of active hydroxyl hydrophilic sites in the polymer. Water also saturated the cell wall and void spaces within the SCB polymer network before reaching equilibrium. The results indicate that SCB polymer network expansion by water reached a maximum when the amount of SCB was about 50 g (optimum). Further increase in the amount of SCB had no substantial effect on water absorbency of the SROFSMP. This could be attributed to the saturation and chain termination of the polymer network, consequently reducing the hydrophilicity of the SROFSMP. Although different solutions (distilled water, tap water and salty water) showed little influence of the amount of SCB in the SROFSMP required to reach swelling equilibrium, distilled water gave higher swelling values than salty water and tap water. This property of water retention is important in many applications especially in agriculture, where SCB can serve as an ideal hydrogel for moisture retention, slow release of the retained water to crops as well as a soil conditioning material.

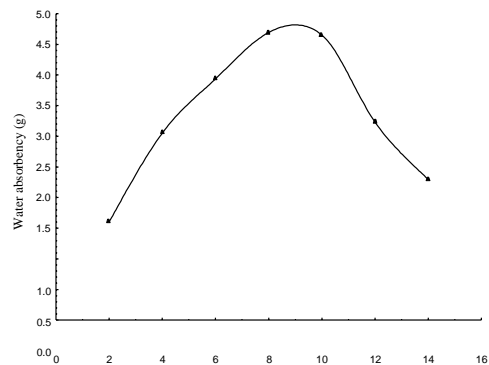


Figure 7: SCB influence on fertilizer QH₂O (g): (a) distilled H₂O; (b) 0.9 %NaCl; (c) tap H₂O

polymers. The effect of the amount of NNMBBA on water absorbency was studied. Figure 7 demonstrates the effect of crosslinker content on water absorbency of SROFMSP in tap water. It can be seen that water absorbency increased with the increase of crosslinker content up to 4.7 g when crosslinker was 8 g, but with higher crosslinker content, water absorbency decreased considerably. Increase in water absorbency with

increasing crosslinker content could be attributed to the lower crosslinking density, with smaller amount of crosslinker, which would cause increase in solubility of the SROFSMP and improvement of the polymeric network in tap water. When the amount of crosslinker was more than 8 g, further increase in crosslinking density of the SCB hydrogel network led to the decrease of space between the three dimensional polymer networks, the resulting structure was unable to expand to hold large quantity of water. Over crosslinking also resulted in reduction of the more reactive hydroxyl sites on the cell wall polymer of SCB, consequently decreasing its hydrophilic property while increasing hydrophobic regions. This made it difficult for the network to be swollen by water, which is responsible for the observed decrease of water absorbency. Thus, the optimum amount of NNMBA was 8 g for SROFSMP development.

Influence of reaction temperature

Reaction temperature is an important parameter in water absorbency. With low temperatures, the three dimensional network of the polymer does

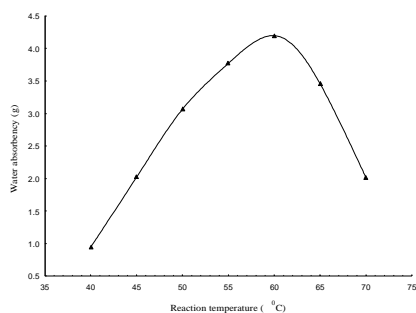


Figure 8: Reaction temperature influence on

fertilizer water absorbency in tap water.

Influence of acrylic acid neutralization by ammonia

The degree of neutralization of acrylic acid by ammonia had considerable effect on the water absorbency of the SROFSMP, as it influences polymerization rate and the charge number in the polymer network. Neutralization degree is the molar percentage of carboxyls in acrylic acid neutralized by ammonia. Ammonia neutralizes acrylic acid, converting the carboxylic acid group into carboxylate group, which sets up an

not fully develop because reaction cannot be entirely complete, while too high temperature would result in over crosslinking of the polymer network. The water absorbency of the fertilizer SROFSMP at different temperatures in tap water was studied. The water absorbency increased with increasing temperature and reached a maximum when temperature was 60 °C, then decreased with further rise in temperature as shown in Figure 8. The increase of water absorbency with temperature increase could be attributed to increase in chain growth, crosslinking reaction and chain termination. Before the temperature reached a maximum of 60 °C, chain length growth was dominant leading to increase in water absorbency. Further increase in temperature led to domination of crosslinking reaction and chain growth termination, so that water absorbency started to decrease with further temperature increase. It is, therefore, important to strike a balance among chain growth, crosslinking reaction and chain growth termination. Thus, the optimal reaction conditions for the preparation of the SROFSMP occur at 60 °C.

electrostatic repulsion, which tends to expand the polymer network that increases water

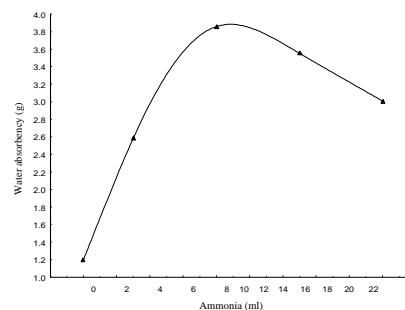


Figure 9: Acrylic acid neutralization influence on fertilizer QH₂O in tap water.

absorbency. It is apparent that water absorbency increased at first with increase in the degree of neutralization and reached a maximum of 3.86 g (Figure 9). This is due to the fact that the activity of acrylic acid is faster than that of acrylate. Increase in polymerization rate, would lead to increase in the soluble part of the SROFSMP (water soluble hemicelluloses) and the content of oligomers. Electrostatic repulsion that tends to expand the polymer network and the osmotic pressure between polymer and the external

solution would also increase. The effect of these factors is an increase in water absorbency. In contrast to this increasing trend, water absorbency decreased gradually from 3.86 g to 3.01 g by further increase in neutralization degree. This could be attributed to increase of the charge density and the content of acrylate as well as the crosslinking density, resulting in tighter network which prevents expansion of the polymer network in tap water, leading to a decrease of its hydrophilicity. This phenomenon could also be attributed to the fact that cooperate absorbing effect between acrylate and acrylic acid groups is superior to that of either group, and therefore, suitable cooperation ration would result in higher water absorbency. It was, therefore, necessary to maintain the degree of acrylic acid neutralization by ammonia at 20:10 per volume for the SROFSMP.

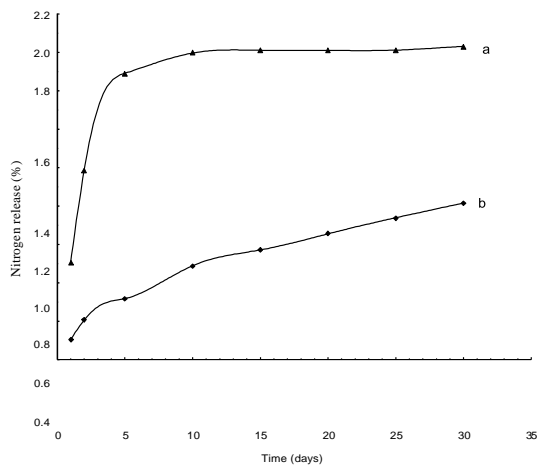


Figure 10: Nitrogen release behaviour in soil:

(a) untreated soil; (b) treated soil.

The release behaviour of P in Figure 11 was similar to that of N. Untreated soil (a) released about 150 mg/kg within 10 days before leveling at day 15. For the SROFSMP treated soil (b), there is a general gradual release of the P component that coincides with plant requirement. This result is similar to release models reported by Liu *et al* (2007) and Wu *et al* (2008).

Nutrient release behaviour of fertilizer in soil

N, P and K release behaviour of the fertilizer in soil was studied and recorded. Release behaviours of the N, P and K of fertilizer treated and untreated soil is shown in Figures 10, 11 and 12 respectively.

All three curves show similarity, with untreated soil (a) releasing most of the available nutrients within the first 5-10 days before slowing down gradually. As shown in Figure 10, the untreated soil sample (a) rapidly released its N within the first five days before leveling off after 10 days at 2.0% N. The fertilizer treated soil (b) showed gradual release, barely releasing about 1.2% N in 30 days. The time of release of N in the fertilizer was within the recommended time; about 80% of active component should be released over a period of 30 days to obtain the desired increase in plant growth.

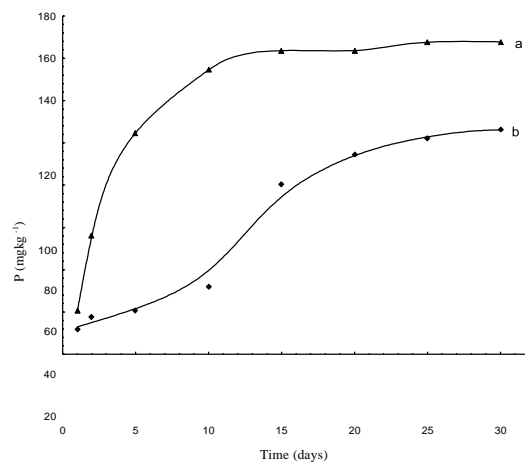


Figure 11: P release behaviour in soil:

(a) untreated soil; (b) treated soil

K release mechanism in untreated soil show fast release rate compared with that of the fertilizer treated soil. As shown in Figure 12, most of the available K in untreated soil (a) was released within 10-15 days (0.22 mg/kg). Fertilizer treated soil (b) posses slow release properties, which released 0.14 mg/kg within the 30th day.

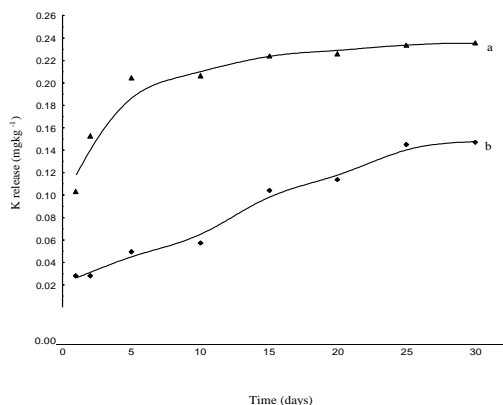


Figure 12: K release behaviour in soil: (a) untreated soil; (b) treated soil

Although release behaviour of conventional fertilizers was not done, studies by Liu *et al.*, (2006) and Wu *et al.*, (2008) show similar release behaviour. Soil treated with SROFSMP showed systematic gradual release of N, P and K with time, which is in accordance with standard slow release fertilizers of the Committee of Europe Normalization. Release mechanism involves three processes. Firstly, the superabsorbent material in the SROFSMP would be slowly swollen and gradually converted into hydrogel by water in the soil. Secondly, water in

Water retention and holding capacity behaviour of SROFSMP in soil

Water evaporation rates of soil containing SROFSMP, SCB and that without sample (control) were studied. The water evaporation rate of soil with fertilizer was lower than that with SCB and control sample as shown on Figure 13. After 35 days, fertilizer treated soil had given off 77.2% while untreated soil had given off 88.8% of its water content. It was also Studies on water holding capabilities of soil containing SROFSMP, SCB and without sample were conducted and summarized in Table 2. These results are an indication that water flow rate in soil was slowed down more by SROFSMP addition to the soil. Water filtration rate in soil containing SROFSMP virtually took almost double the amount of time taken by SCB and almost three times

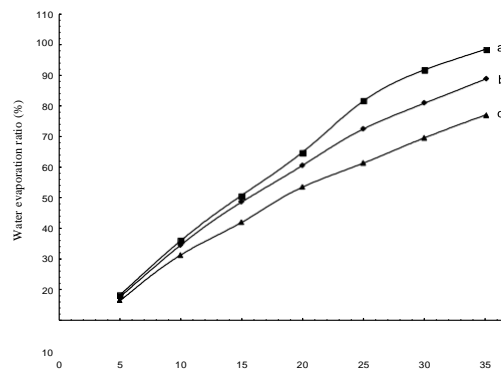


Figure 13: Water evaporation ratios: (a) control sample (b) soil with SCB (c) soil with fertilizer

that of control sample. the swollen polymer network would slowly dissolve nutrients present, creating a dynamic exchange between water in the polymer network and water in the soil. The dissolved nutrients would then diffuse slowly into the soil, creating a slow release property of the fertilizer. In the slow release process, water penetrates through the polymer network into the inside of the fertilizer granules. Nutrients then dissolve, and the resulting osmotic pressure leads to swelling of the polymer matrix, which then allows ion transport into the soil.

observed that soil containing fertilizer SROFSMP and SCB had granular structures while that without sample hardened after 30 days. These results were an indication that the prepared SROFSMP sample had water retention and moisture preservation capabilities. With the fertilizer, polymer network within SCB could absorb and reduce water evaporation. The absorbed water would then be released slowly as evidenced in the study, giving plants ability to withstand harsh environmental conditions.

Water holding ration was also higher in SROFSMP soil. The observed behaviour was attributed to the superabsorbent and moisture preservation properties of the polymer network within the SROFSMP. These properties are important, that could find great application in dry and arid areas or even reduce irrigation frequency in farmlands for sustainable crop production.

Table 2: Water holding and infiltration rate in soil.

Sample	H₂O holding ratio (%)	Infiltration rate (min)
SROFSMP	40.6	2.30
SCB	36.6	1.50
Control sample	25.4	0.93

Micronutrient (Fe, Zn and Cu) analysis by AAS

Fe, Zn and Cu analysis of the SROFSMP and SCB sample was done to determine their availability for plant uptake and their potential or environmental contamination (Table 3). An appreciable effect of heavy metals in the fertilizer on crops can however be attained from precise knowledge of the heavy metal speciation and the response to plant species. In addition, speciation can determine metal mobility and hence

potential contamination of ground water following fertilizer application.

Zinc

The use of zinc fertilizers in zinc-deficient soils can increase crop productivity as well as the zinc nutritional status of the crops. In the SROFSMP and SCB samples studied here, the zinc values (395.56 mg/kg and 344.07 mg/kg respectively) recorded were higher than both the recommended (150 mg/kg) and the maximum (300 mg/kg) permissible values.

Table 3: Micronutrient levels in SROFSMP and SCB

Micronutrient	SROFSMP	SCB
Fe (mgkg ⁻¹)	5837.04	8514.81
Zn (mgkg ⁻¹)	395.56	344.07
Cu (mgkg ⁻¹)	59.26	629.63

Iron

The calculated values in mg/kg present in the fertilizer and SCB samples were 5837.04 mg/kg and 8514.81 mg/kg respectively. These values analyzed in the fertilizer and SCB samples are above the iron threshold values (> 10 ppm) in soil for plant uptake. However, low plant-availability has been reported in many

environments despite high total Fe concentrations in the growth medium. Availability depends on properties of the solid phase (mineral source, other factors), pH, Redox potential and presence of chelating agents.

Copper

The amount of Cu available for plants varies widely by soils from 1 to 200 mg/kg in both mineral and organic soils as a function of soil pH and soil texture. The finer-textured mineral soils generally contain the highest amounts of Cu. The lowest concentrations are associated with the organic or peat soils. In this study, the levels of copper detected in the fertilizer (59.26 mg/kg) are therefore within the recommended range for plant uptake. Levels in the SCB sample (629.63 mg/kg) are however beyond recommended values and may prove toxic depending on the soil condition. In the SCB sample for example, amounts of Cu available for crop uptake would be low due to the high SCB pH level.

Incidences of micronutrient deficiencies in crops has increased markedly in recent years due to intensive cropping, loss of top soil by erosion, losses of micronutrients through leaching, liming of acid soils, decreased proportions of farmyard manure compared to chemical fertilizers, increased purity of chemical fertilizers, and use of marginal lands for crop production. Micronutrient deficiency problems are also aggravated by the high demand of modern crop cultivars. In this study, the amounts of Zn, Fe and Cu in the developed fertilizer represent an ample opportunity to replenish micronutrients for sustainable and better crop production. The extractable amounts of the micronutrients available to plant however depend on soil properties and other factors such as pH, organic carbon and clay content. Therefore, micronutrient recommendations are based on soil and plant tissue analyses, the crop species and expected yield, management level, and research results. In this study, the slow release property, the suitable pH level (7.7) and soil granular structure associated with the fertilizer would facilitate uptake of micronutrients by crops without the required resistance to sudden change in pH.

CONCLUSION

A slow release fertilizer with superabsorbent and moisture preservation properties was prepared from sugarcane bagasse, a lignocellulosic waste

of sugarcane industry. Sugarcane bagasse was the source of the organic material and *N*, *N'*-methylene-bis-acrylamide as the cross-linker. The cross-linker allowed formation of the three-dimensional network of the fertilizer, which allowed water retention and releasing the water when needed. The fertilizer treated soil showed gradual release of nutrients, releasing 1.2 % of nitrogen in within 30 days while the untreated soil rapidly released its nitrogen within the first five days. Similarly, the fertilizer treated soil released K and P gradually compared to the untreated soil. Micronutrient analysis revealed that the fertilizer contained 5837 mgkg⁻¹ of Fe, 396 mgkg⁻¹ of Zn and 59 mgkg⁻¹ of Cu. The values of zinc are higher than the recommended value of 300 mgkg⁻¹ and are therefore toxic. However, the amount of iron and copper were within the recommended levels.

Thus, the fertilizer displayed superior properties such as slow release, superabsorbent and moisture preservation capabilities. It is also endowed with high micronutrient and nutrient levels. As a result, it is a potential bio-fertilizer that can be used in areas that experience low rainfall patterns.

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