Development of a Multi-Nutrient Fertilizer from Liquid Waste of Solar Salt Manufacturing Process

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Abstract— **Magnesium plays a key role in the growth of a plant by acting as the central atom of the chlorophyll molecule. This study is carried out to develop a low-cost multi-nutrient fertilizer by utilizing the bittern solution. This fertilizer is capable of fulfilling the Magnesium, Potassium and Calcium requirement of a plant effectively. A dilution series of bittern was prepared, and a series of tests was carried out to demonstrate the importance of multi-nutrient fertilizer to the growth of a plant. This fertilizer contains 1.27%, 0.31% and 0.01% of highly water soluble Magnesium, Potassium and Calcium respectively to cater the short term requirement of a plant.**

Developing an indigenous source of supply for fertilizer is important both for the agricultural and strategic reasons. The major drawback of conventional salt production has been overcome by using bittern to produce a multi-nutrient source for plants. It could also mitigate negative environmental impacts by successfully controlling pollutant discharge. Therefore, this novel process can be considered as a comprehensive solution towards sustainable development.

Key Words – bittern, fertilizer, magnesium, multi-nutrient, potassium

I. Introduction

As an island that gets sunlight throughout the year and solar evaporation is the most effective and the cheapest method to produce salt in Sri Lanka. The country produces approximately 100,000 metric tons of salt per annum. The extraction of salt from sea water consists of progressive evaporation of brine in large ponds. As the brine evaporates, its concentration increases and constituents crystallize. Usually, Sodium Chloride is crystallized from brine between the densities of 24 Be^o and 29 Be^o [1]. Once the Sodium Chloride fraction is separated from the brine over affixed concentration range, the remaining mother liquor is called as "bittern". During the conventional salt production process, bittern is returned back to the ocean without consuming it for further manufacturing processes. The bittern contains significant amounts of Magnesium, Potassium, and Calcium ions. Since the bittern consists of high concentration of soluble ions, once it is deposited back into the ocean it causes an osmotic shock to the multitude of living organisms in the inshore waters. For this reason as an effluent of the salt industry, the release of bittern to the ocean causes negative environmental impacts.

Magnesium plays a vital role in the growth of plants. It is the central atom in the chlorophyll molecule, which photosynthesis depends on (Fig.1). Chlorophyll formation, synthesis of amino acids and cell proteins and uptake of phosphorus in plants are some of the major contributions of Mg. Potassium is also an essential nutrient for plant growth that is required in large amounts. Enzyme activation, photosynthesis, transport of sugars, water and nutrient transport, protein synthesis and starch synthesis are some of the major roles of Potassium in plants.

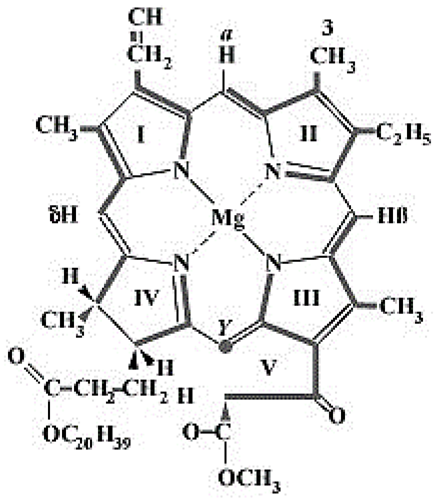

FIG.1 CHLOROPHYLL MOLECULE

Evaporation - crystallization, cooling - crystallization, solvent extraction, ion exchange and salting out are the primary methods that have been used to recover chemicals from the sea water bittern in the industry [2], [3]. Different methods to recover Mg, K and B from bittern as PO_4 complex salts have also been carried out [4], [5], [6], [7], [8], [9].

The primary objective of this research is to determine the optimum dosage of sea water bittern which could be used to cater the short term requirement of Magnesium, Potassium, and Calcium to a plant. In Sri Lankan context, there is a huge demand for a low-cost multi-nutrient fertilizer that could be used to cater both the short term and the long term requirement of a plant. Therefore, this research can be further extended to develop a multi-nutrient fertilizer utilizing the bittern solution along with dolomite. Bittern solution could be amalgamated with dolomite which is a low-cost mineral powder readily available in Sri Lanka. Dolomite is generally added to soil to raise pH to the range of 5.5 to 6.5. It supplies plants with both Calcium and Magnesium while slowly dissolving in the growth medium over time. Therefore, dolomite is well suitable for long term crops since fertilizer being available for later stages of crop development [10].

II. NOMENCLATURE

NGR	-	Net Assimilation Rate
LAR	-	Leaf Area Ratio
RGR	-	Relative Growth Rate
EDTA	-	Ethylenediaminetetraacetic acid
TSS		Total Suspended Solids

III. THEORY

A. Analysis of plant growth rate

When considering the plant growth, Relative Growth Rate (RGR) can be identified as one of the important parameters. RGR is defined as;

$RGR = NAR \times LAR$ where;

Net Assimilation Rate (NAR) measures the photosynthetic efficiency of plants [11]. It is defined as the biomass increment (dW) per unit time (dt) and then divided by leaf area (A) [12]. Over a short time interval (t_1 to t_2 days) and whole-plant biomass and leaf area are linearly related by,

$$NAR = \left(\frac{W_2 - W_1}{t_2 - t_1}\right) \times \left(\frac{(ln\, A_2 - ln\, A_1)}{(A_2 - A_1)}\right) \text{……………….Equation 1}$$

Leaf Area Ratio (LAR) is defined as the proportion of plant biomass invested in leaf area. It is also considered as a measure of the efficiency that a plant allocates its photosynthetic resources. LAR is directly affected by the light intensity and is increased by low light intensities.

$$LAR = \frac{1}{2}\left(\frac{A_1}{W_1} + \frac{A_2}{W_2}\right) \text{…………………………….Equation 2}$$

Therefore;

$$RGR = \frac{1}{2}\left(\frac{A_1}{W_1} + \frac{A_2}{W_2}\right)\left(\frac{W_2 - W_1}{t_2 - t_1}\right)\left(\frac{(ln\, A_2 - ln\, A_1)}{(A_2 - A_1)}\right) \text{……..Equation 3}$$

IV. METHODOLOGY

A. Analysis of bittern solution

Bittern solution, which is used as the main ingredient of the fertilizer was collected from a saltern in Puttalam – Sri Lanka. Ethylenediaminetetraacetic acid 99.5% (w/w), Calcium carbonate 97%(w/w), Hydroxynaphthol blue, Eriochrome black T, pH 9.2 buffer solution (MERCK chemicals), Hydrochloric acid 33% (w/w), Sodium hydroxide 98% (w/w) and Barium chloride were used for the quantitative analysis of bittern solution.

A vacuum filter unit was set up with Whatman grade 1 (11µm) filter paper which frequently used for qualitative analytical separations for precipitates was used to determine the amount of precipitates produced after treating the bittern solution.

EDTA (Ethylenediaminetetraacetic acid) solution was prepared for the analysis of Ca^{2+} and Mg^{2+} content in the bittern solution. Four grams of EDTA was dried for 1hour at 80°C and allowed to cool to room temperature in a desiccator. 3.8g of dried EDTA powder was added to 100ml volumetric flask and dissolved in distilled water to make a diluted solution. EDTA solution was standardized using calcium carbonate solution.

To produce calcium carbonate solution, primary $CaCO_3$ powder was dried overnight at 110°C. 0.25g of dried $CaCO_3$ was transferred to a 250ml volumetric flask and dissolved using 5ml of 1M HCl solution. Then the solution was diluted to a volume of 250 ml using distilled water. Concentration of the standard calcium solution was calculated. EDTA solution was titrated against the standard calcium solution in the presence of hydroxynaphthol blue as the indicator at a pH of 12 (color change was pale red to blue).

Bittern solution was diluted four times and filtered using dried and pre-weighted filter paper. Then the filter cake was dried in an oven at 110°C until it gives a constant weight over the time and total suspended solids (TSS) content was calculated.

Filtered bittern solution was used to determine the content of ions namely, Mg^{2+}, Ca^{2+} and SO_4^{2-}. EDTA titration method was used to determine the Mg^{2+} and Ca^{2+} content. Ca^{2+} was determined in the presence of the indicator hydroxynaphthol blue at pH 12 where Mg^{2+} was precipitated as $Mg(OH)_2$ and it would not react with EDTA. Then another sample of bittern solution was titrated with EDTA solution in the presence of the indicator eriochrome black T at pH10 to measure the summation of Ca^{2+} and Mg^{2+} present in the solution. pH 9.2 buffer solution was used to maintain the pH of the solution at 10.

In order to determine the SO_4^{2-} content, gravimetric precipitation was used. 250 ml of the diluted bittern solution was transferred to a Pyrex beaker and pH of the solution was adjusted below 3.0 using HCl solution. Equal amount of saturated $BaCl_2$ solution was added to the salt solution while it boiled. Then the solution was mixed well using magnetic stirrer and allowed to digest the solution for 2 hours at 90°C. Digested solution was filtered using vacuum filter. Then the filter cake was dried in an oven at 110°C until a constant weight given over the time. $BaSO_4$ precipitate was then calculated.

B. Bittern dosage optimization

Ten pots of green gram plants were cultivated in identical soil cultures (Fig. 2). In every pot there were four plants which are comparatively similar in size. After growing the plants for a period of one week, two plants were removed from each pot and the average surface area of the plant leaves (A_1) were measured. In order to measure the area of the plant leaves, they were kept over a graph paper and the numbers of squares covered by each and every leaf were count (Fig.3). Then, the plants were dried in an oven until it gave a constant weight to remove all moisture contained with the plant. Weight of the dry plants (W_1) was then measured.

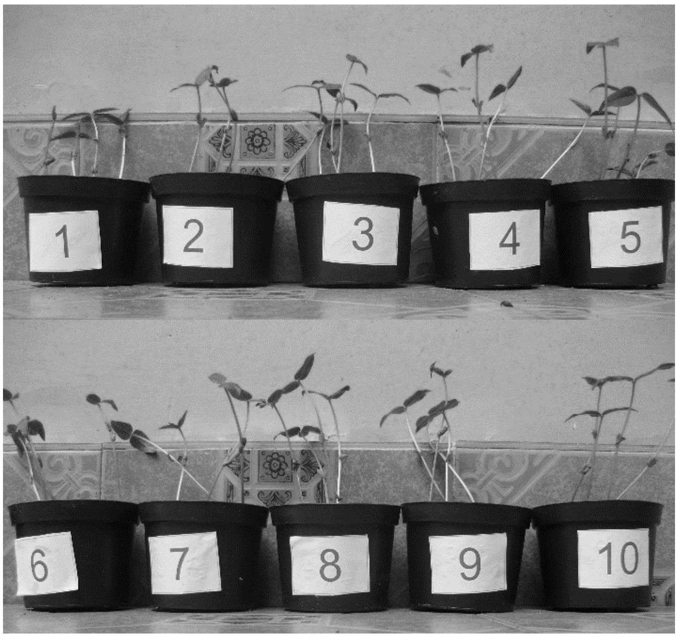

FIG.2 POTS OF GREEN GRAM PLANT USED FOR THE EXPERIMENT

Then the remaining plants were treated with the same amount of bittern solution with varying concentration and allowed to grow for another period of one week. At the end of the second week, surface area of the plant leaves (A_2) and the dry weight of the plant material (W_2) were re-measured following the same procedure. With using the results, NAR and LAR were calculated for the plants in all ten pots. Finally, the Relative Growth Rate is calculated for the plants at the end of second week using the NAR and LAR values obtained and the results are summarized in table II. Depending on the growth rate of the plant, optimum dosage of bittern solution was determined.

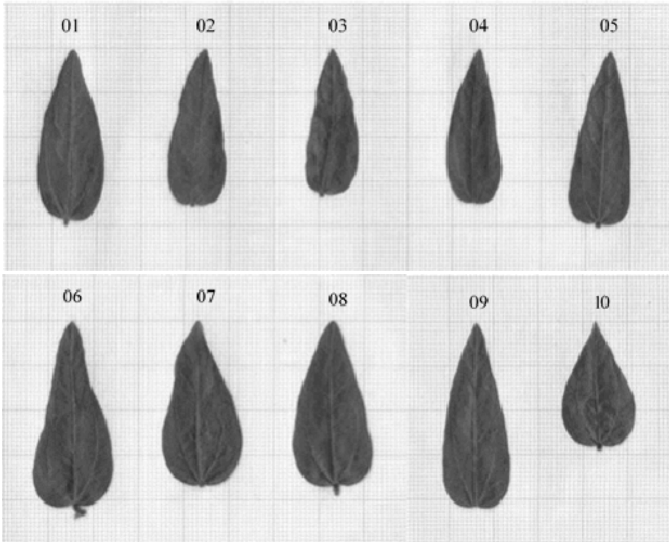

FIG. 3 SURFACE AREA OF THE PLANT LEAVES WERE MEASURED

V. RESULTS AND DISCUSSION

A. Composition of bittern solution

Analysis results for bittern solution prove that there is a considerable amount of Mg^{2+} ions available in it. Furthermore, it contains considerable amounts of SO_4^{2-}, K^+ and Ca^{2+}.

Table I Concentration of ions in bittern solution

Ion	Content (ppm)
Mg^{2+}	31740
Ca^{2+}	150
SO_4^{2-}	43230
K^+	7630

B. Relationship between bittern dosage and plant growth rate

Plant growth rate is represented by three main parameters namely, NAR, LAR and RGR. Table II is tabulated with the results for these parameters for the plant species at the end of first and second weeks.

Fig 4 describe the effect of bittern dosage towards the NAR of the plant species. According to the graph, it has the maximum NAR value with a bittern dosage of 400 ppm. This result implies that the photosynthetic efficiency of the plant species is maximum with a bittern dosage of 400 ppm. According to the Fig 5, LAR of the plant species under the same bitter dosage results a minimum and interpret it has a good photosynthetic efficiency with the lowest leaf area compared to the other samples under different bittern dosages.

According to the Fig 6, it is possible to observe positive trend for RGR in the range of 0-390 ppm of bittern. It is also possible to observe a maximum at 390 ppm of bittern and then a negative trend. Finally, the RGR is independent of bittern dosage above 780 ppm.

Therefore, after considering the behavior of all these parameters it can be concluded that the optimum dosage of bittern for the plant species as 390 ppm.

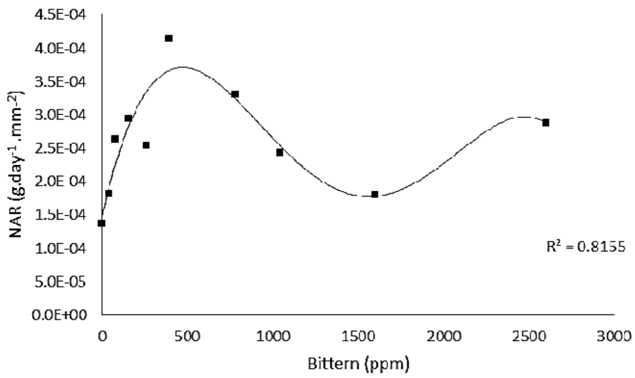

FIG. 4 EFFECT OF BITTERN DOSAGE ON NET ASSIMILATION RATE

TABLE II RGR OF PLANT

Plant Number	Bittern (ppm)	A_1 (mm^2)	W_1 (g)	A_2 (mm^2)	W_2 (g)	NAR ($g.day^{-1}.mm^{-2}$)	LAR ($mm^2.g^{-1}$)	RGR after two week ($g.g^{-1}.day^{-1}$)	
1	0	377	0.383	1700	1.227	0.0001	1184.8707	0.1627	16.27%
2	39	296	0.341	1580	1.320	0.0002	1032.4431	0.1884	18.84%
3	78	287	0.408	1418	1.716	0.0003	764.9160	0.2019	20.19%
4	156	349	0.486	1677	2.236	0.0003	734.1652	0.2169	21.69%
5	260	418	0.392	1766	2.056	0.0003	962.6114	0.2446	24.46%
6	390	461	0.550	1176	2.764	0.0004	631.8398	0.2618	26.18%
7	780	441	0.604	1040	2.224	0.0003	598.8382	0.1985	19.85%
8	1040	466	0.577	1545	2.113	0.0002	769.4082	0.1876	18.76%
9	1600	459	0.442	1707	1.644	0.0002	1038.4615	0.1877	18.77%
10	2600	314	0.466	1221	1.812	0.0003	673.8197	0.1940	19.40%

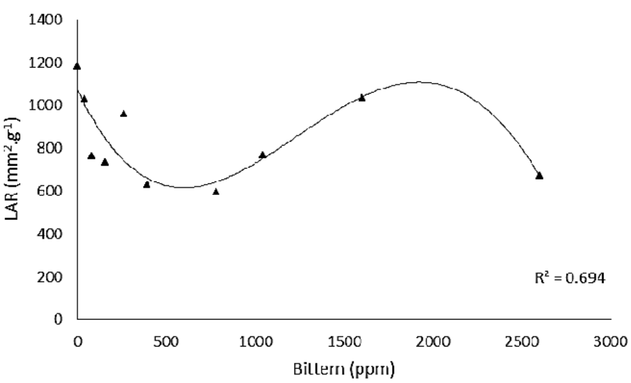

FIG. 5 EFFECT OF BITTERN DOSAGE ON LEAF AREA RATIO

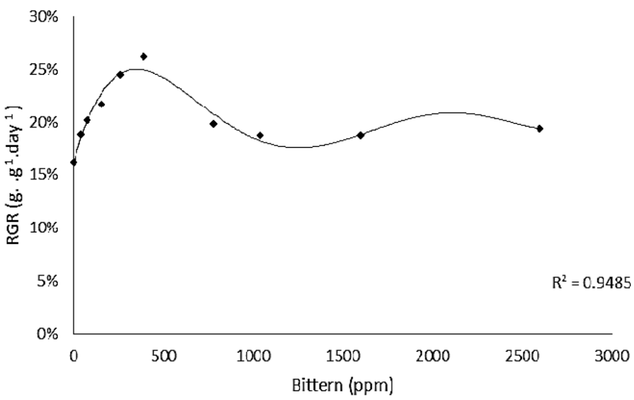

FIG. 6 EFFECT OF BITTERN DOSAGE ON RELATIVE GROWTH RATE

VI. CONCLUSION AND FURTHER WORKS

Bittern solution which is a byproduct of solar salt production process can be used as a reliable source of predominantly Mg and other nutrients required for plants. The findings of this research can be used to develop the agriculture sector of Sri Lanka considering the fact of the competitive advantage prevails in the country with abundant of solar energy and sea water around the country. Utilizing bittern as the raw material for a fertilizer will save large amount of foreign exchange draining out from the country and prevent discharging of highly concentrated salt solution to coastal areas which causes a significant environmental impact.

According to the results tabulated in Fig. 4, optimum bittern dosage was determined as 390 ppm. Still the product should be developed to a form of fertilizer which has a higher level of efficiency on delivering nutrients to the plant.

According to the literature, magnesium can be supplied as slightly water soluble form when the magnesium content in soil is less than 100 ppm. When the magnesium content in the soil is below 20ppm, it is recommended to supply magnesium in highly water soluble form [13]. Therefore, this multi-nutrient fertilizer could be able to apply under either of these circumstances.

Dolomite is identified as a suitable mineral to be used in this process to fulfill the long term Magnesium requirement. It is produced in Sri Lanka and available for very low cost and even when the bittern is mixed with dolomite, surface area available for drying is also get increased and therefore the efficiency of solar drying is also increased. Therefore, it is possible to develop the multi-nutrient fertilizer in the form of solid for a lower cost.

Further studies are currently carrying out to determine the optimum dosage of Dolomite needed to be mixed with bittern solution. This combination should be selected considering the norm of requirement of Magnesium and other fertilizer for the crops, solar drying efficiency of the mixture and the economic aspect.

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