DETERMINATION OF RELEASE RATES OF CONTROLLED RELEASE KCL FERTILIZER.

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Abstract

Network Controlled and slow release fertilizer can increase K use efficiency and reduce environmental contamination ,but accurate prediction of release rates is needed.Sand matrix based KCl controlled release fertilizer is made and tested. The parameters of the study are initial fraction of KCl, fractional binder, Fractional inert, Diameter of the pellet and Particle size of the sand. The release of fertilizer from the pellet depended on the compositional parameters of the study

Keywords: Plant nutrients, fertilizer, controlled release, modeling, naphthalene, KCl

Application of fertilizers is inevitable in the modern farm practice to get better yields. Fertilizers add nutrients to the plants those are not adequately supplied by the soil. Fertilizers are classified into two broad groups namely organic and inorganic. Organic fertilizers are derived from living resources like plant or animal. For example: manure, sewage sludge, blood meal, cotton seed meal and bone meal etc. Chemical fertilizers are manufactured synthetically and have many advantages like it could be manufactured at a very fast rate and also at low cost. The fertilizer could be supplied to the plant at a very faster rate but some times the release is too fast need to be controlled for several reasons as discussed below.

Since the solubility of chemical fertilizers is very high leads to the condition of abundant supply of nutrient to the plant which in turn causes root burn and finally damage the plant. Increased intake of fertilizers is highly susceptible for the attack of pest. In addition to the problems mentioned above, cost of the produce is high with the increased use of fertilizer. The other unwanted conditions are loss of fertilizer by way of leaching leads to the ground water pollution. To overcome the above problems the use of controlled release fertilizers are recommended. Controlled release fertilizers are broadly defined as products that release nutrients to the soil for plant uptake at a pre-determined time and rate.

The application of controlled release fertilizers have following objectives

1.To improve the yield and reduce the cost of production.

2.To increase the nutrient efficiency and quality of the produce.

3.Reduction of plant toxicity and stress.

4.Substantial reduction in ground water pollution and water bodies.

5.Reduction of the labor cost for the application of fertilizer.

Application of controlled release fertilizer could achieve the following advantages

1.Root burn can be avoided with the application of controlled release fertilizers even at the increased quantities of fertilizers supplied.

2.Fertilizers are released at a slower rate throughout the season; so that plants could take up most of the nutrients without much waste by way of leaching.

3.Reduced seed or seedling damage from high local concentrations of salts

4.Reduced leaf burn from heavy rates of surface application.

Application of controlled release fertilizers has several advantages. Despite the several advantages of controlled release fertilizers, only about 0.15% (Dr. Sunil K. Jain reviewed the controlled release fertilizer withcoating65)of the total fertilizers consumption is controlled release fertilizers. This is mainly due to the very high cost of Controlled release fertilizers and lack of proper legislation in many parts of the world.

Hence, the development of cost effective controlled release fertilizers have been a never ending quest for scientific community and a delight to the farmers as it offers several advantages over conventional fertilizers.

In India, the farming community made several attempts to develop the controlled release fertilizers and practiced. The methods they adopted were tar coated urea; neem cake mixed with urea and urea coated with neem seed extract and were practiced. The farmers found difficulty in the preparation of tar coated urea and urea coated with neem extract as it resulted uneven and uncoated urea. For the case where urea mixed with neem cake has very low retention capacity because of its high porosity. The practice of neem extract coated urea was failed because of tedious procedure required for it. The methods available so far failed due to one or other reasons. Due to the above reasons an attempt is made in the present study to develop a controlled release fertilizer.Sixteen nutrient elements are essential for the growth and reproduction of plants. Plants obtain the most abundant nutrients – carbon, hydrogen and oxygen – from water and the air. The other 13 elements are divided into three categories: primary, secondary and micronutrients. Nitrogen (N), phosphorus (P) and potassium (K) are primary nutrients which are required in fairly large quantities compared to the other nutrients. Calcium (Ca), magnesium (Mg) and sulfur (S) are secondary nutrients needed for the plant in lesser quantities than the primary nutrients. Zinc (Zn), manganese (Mn), iron (Fe), boron (B), copper (Cu), molybdenum (Mo) and chlorine (Cl) are micro- nutrients which are required by plants in very small quantity. The primary and secondary nutrients are required in large amount. These are said to be as macro nutrients, Among them KCl is an important fertilizer applied to water logged rice fields which is liable to loose through run of water because of its instantaneous nature of dissociation and high mobility.

Some of the KCl fertilizer also lost through seepage. To retain the KCl fertilizer for longer time in the field, it is necessary to develop a controlled release fertilizer. Hence an attempt is made in the present study to develop controlled release potassium chloride fertilizer.

The aim of the study is to develop cost effective controlled release potassium chloride fertilizer and evaluate its release rate and release fraction with time. It is further proposed to develop a model and compare the results with the model developed. Potassium chloride, sand and plaster of paris system was envisaged, with which controlled release fertilizer pellets are made with sand matrix and plaster of paris as a binder. The sand is present everywhere on the earth and is available to the farmers at free or negligible cost, so that the controlled release fertilizers could be prepared at less cost.

Among the several binders considered for the pellets preparation, plaster of paris was chosen because of its availability at moderate costs. It also has very good binding capacity with sand in the preparation of aggregate. As the materials used for the preparation of the aggregate are familiar to the farmers, the procedure developed can be easily implemented. The pellets prepared are of various composition of KCl, sand and plaster of paris .

The binder fraction in pellet was maintained in the range from 0.05 to 0.3. However lower binder fractions were favored on cost consideration. The binder fractions beyond 0.3 were found to be unsuitable as the pellets so made were unable to release the KCl. The data are analyzed and the results obtained are presented in terms of time Vs fraction of fertilizer retained in pellet (XA) and release rate (-rA). The results revealed that the pellets prepared in the present study could last up to 18 days. The study was also directed to conduct experiments with pellets of reduced release by incorporating pore blocking agents like benzoic

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acid. Dissolution studies of these pellets resulted slow release fertilizers. Benzoic acid based fertilizer lasted for 38 days. Thus the controlled release fertilizers produced are highly useful for the farming community.

Based on Fick`s second law, a model was developed for the above controlled release fertilizers. The data simulated from the model is in good agreement with experimental values. The developed model constituted with correction factor (ml) parameter together with other parameters is highly useful for predicting the release rate data. The controlled release fertilizers can be prepared using the above knowledge.

The developed equations are as follows:

With coating : XA =gt = 3 [Dt (cs)]
0 <t< Y

ρsr (lcml)

XA=gt=1-cs/ρsexp [-3D/rlc(t-Y)] t>Y

Where lc depends on system of the study and its parameters.

The Values of ml for each system is presented under

ml = 0.52488 fkcl0.8 f -0.32 fs1.75 fd-0.19-- Benzoic acid coating

MATERIALS AND METHODS

Materials

Materials used in the present study are classified into two groups. The first group is those principally used for the preparation of pellet either in making pellet matrix or coating material. The second groups of materials are utilized in analysis of the leachant.

The first group or pellet forming materials are as follows.

1. Potassium chloride (fertilizer)
2. Sand (inert material)
3. Plaster of paris (binding agent)
4. Naphthalene coating material

Potassium chloride utilized in the present study is an analytical reagent whereas sand is of river bed origin washed number of times followed by drying in oven at 110 oC for four hours. Plaster of paris utilized in the preparation of pellet is Gypsum plaster. The chemicals used for the pellets of coatings are wood polish and naphthalene is of commercial grade. The other chemical employed as coating material is analytical grade Benzoic acid.

Chemicals used for the analysis of the leachant are presented here under.

1. Silver Nitrate AR
2. Potassium chromate AR
3. Sodium chloride. AR

Properties and uses of various other materials utilized in the present study are presented hereunder.

Potassium Chloride

Potassium Chloride is fertilizer or active ingredient in the present study. Analytical grade Potassium Chloride was incorporated in the pellet. It is a primary nutrient and is necessary for the healthy growth of the plant. Potassium chloride (KCl) is a fertilizer which is most conveniently expressed as K2O. It is made by the reaction of hydrochloric (muriate) acid on potassium containing materials. It contains about 63.17% K2O and K content of about 52.44%. It is also known as the muriate of potash.

Potassium is readily absorbed and may accumulate in plant tissue greater amount than actual crop requirement. Potassium is relatively mobile in acidic sands under high rainfall conditions. Particularly it is mobile where the application of ammonium salts is more. In some cases, soluble potassium salts may be toxic if ionic concentration is high enough to interfere with water uptake by the crop. Under these conditions, controlled release potassium is beneficial. KCl is highly soluble in water as it readily dissociate in water, is liable for loss with water either by seepage or by drainage. Hence KCl has been selected for the development of controlled release fertilizer. Controlled release fertilizer pellets were prepared with varying proportions KCl, inert and binder proportions.

Sand: Sand is selected as inert matrix or barrier material for the release since it is cheap and shows a tendency to form aggregate with cement, makes it suitable for the matrix material in the present study. It is cheap and easily available for farmers as it may be procured from neighboring streams. It is generally a part of soil, so that no unwanted residue is left in the field unlike controlled release fertilizers made with polymer coating. Sand matrix has the advantage of negligible cost as it can be procured from neighboring streams at meager cost.

Plaster of paris: Several binding agents were visualized for the study. Among them sodium silicate, tar, cement, lime and cement are prominent. But plaster of paris binder was selected for the study as it is available abundantly to farmers at fairly cheaper price. Hence plaster of paris sand system was selected for the study.

Coating Materials

Naphthalene

Naphthalene, also known as naphthalene, bicyclo[4.4.0]deca-1,3,5,7,9-pentene or antimite, is a crystalline, aromatic, white, solid hydrocarbon with formula C10H8 and the structure of two fused benzene rings. It is best known as the traditional, primary ingredient of mothballs. It is volatile, forming a flammable vapor, and readily sublimates at room temperature, producing a characteristic odor that is detectable at concentrations as low as 0.08(gm mole/lit). A naphthalene molecule is derived by the fusion of a pair of benzene rings. (In organic chemistry, rings are fused if they share two or more atoms.) Accordingly, naphthalene is classified as a benzenoid, polycyclic aromatic hydrocarbon (PAH). There are two sets of equivalent hydrogen atoms: the alpha positions are 1, 4, 5, and 8 on the drawing below, and the beta positions are 2, 3, 6, and 7. unlike benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are about 1.36 Å (136 pm) in length, whereas the other carbon-carbon bonds are about 1.42 Å (142 pm) long. This difference, which was established by x-ray diffraction is consistent with the valence bond model of bonding in naphthalene that involves three resonance structures (as shown below); whereas the bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in two of the three structures, the others are double in only one. Like benzene, naphthalene can undergo electophilic aromatic substitutuon. For many electrophilic aromatic substitution reactions, naphthalene reacts under mild conditions than doe's benzene. For example, both benzene and naphthalene react with chlorine in the presence of a ferric chloride or aluminum chloride catalyst. Naphthalene and chlorine can react to form 1- chloronathalene even without a catalyst. Similarly, whereas both benzene and naphthalene can be alkylated using reactions. Naphthalene can also be alkylated by reaction with alkenes or alcohols, with sulfuric or phosphoric acid as the catalyst. It is normally used as a chemical intermediate, wetting agent/surfactant and also as a fumigant.

Preparation of Potassium chloride pellets

Controlled release Potassium Chloride fertilizer pellets were made with sand- plaster of paris composite as an inert matrix. Plaster of paris was chosen as binder because of its availability and low cost. The initial fraction of Potassium Chloride in the pellets was varied as 5, 10, 15, 20, 25 and 30 percent. Plaster of paris composition was varied as 5, 10, 15, 20, 25 and 30 percent. The sand composition was varied as the binder and inert materials together contribute to inert matrix. The particle size of sand was also varied as it alters the porosity of the pellet which affects the diffusion rate. The sand particle sizes of 250 □m, 212□

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The ranges of variables covered in the present study are presented as table5.1.

In the present study, the pellets of Potassium Chloride (KCl, sand &plaster of paris system) were prepared by mixing Potassium Chloride with sand and plaster of paris in the ratios of 5:95, 10:90, 15:85,20:80,25:75,30:70. The inert composition was also varied to obtain varied strength to the pellets. The proportions of the sand-plaster of paris - fertilizer ratios are maintained as 70:30, 75:25, 80:20, 85:15, and 90:10, 95:5. The ingredients of the pellet were mixed with minimum amount of water in a ceramic crucible and moulded into spherical pellets. The mould sizes were varied as 1cm, 0.75cm, and 0.5cm. Larger particle sand sizes are made as they are not suitable for fertilizer applications. Small size pellets were not attempted as they are limited to shorter time of release. The size of the pellet was also limited by the size of the constituent sand particles. The pellets were cured and dried in shade for 10 days. The procedure was repeated to prepare pellets with different sizes sand particle.

Procedure for Pellet Coating

Phase inversion technique was used for pellets coating with benzoic acid and naphthalene. The coating chemicals were dissolved separately in kerosene till the saturation condition was attained. The pellets were dipped in saturated solution followed by drying at 600C for one hour. All the kerosene was evaporated leaving behind the coating materials inside the pores of the pellets. For the wood polish coated pellets were dipped in polish followed by drying at room temperature.

Dissolution Procedure

Pellets of known composition were taken in separate 500ml beakers to which 200ml of water was added. The leaching takes place as the time progresses. The solution was stirred gently and 1ml of the leachant sample was taken and transferred into a conical flask to which 10ml of distilled water was added. One ml of distilled water was added soon after the leachant sample was taken out of the beaker. The beaker was closed with a lid to avoid loss of water by evaporation. Similar procedure was ☐repeated for the pellets in other beakers also.

m were used for the preparation of pellets.

The samples were tested for KCl content by volumetric analysis by titrating against silver nitrate solution. Samples of leachant were collected from time to time and tested for its KCl concentration. The time verses concentration of potassium chloride in the leach liquor was obtained for the pellets with and without coating. The concentration data was taken for 20 days for the pellets without coating. The release data was extended for a maximum period 40 days in the case of pellets with coating.

porosity Measurement

Sample pellet was taken and weighed for its initial weight (w1). The sample was then placed in a petre dish and was saturated with water. Excess amount was wiped out with filter paper. The weight of the pellets was again taken (W2). Difference in weight is the weight of water adsorbed. The porosity of the pellet was measured as given below.

Porosity ε =(w2-w1)/w1.

☐☐☐☐ w2 ☐ w1

= Δw / w1

W1

☐ ☐porosity

Measurement of Coating Thickness

Film thickness of benzoic acid was measured by weight difference method. Thickness of pellets Coating: (lc)

Initial weight of the of the pellet = w1c Radius of the pellet (initial) = r1

Initial volume of the pellet = (V1) Weight of the pellet after coating = w2c Change in weight =w2c-w1c =Δwc

Where ρ is the density of the coating material Volume of Coating = V2= Δwc/ρ

Total pellet Volume = V1+ V2 = VT

Increase in radius is obtained from the following expression v □□□□□□ □□r2 3)

Where r2 is radius after coating

The total volume of the pellet multiplied with porosity of the pellet will get pore volume Porosity = ε

VT = (4/ 3) × □ r2 3 × ε

From above equation will get r2 r2 - r1 = lc

From equation will get thickness of the coating.

Classification of Controlled release fertilizer

Controlled release fertilizers are classified as follows:

Natural Organics: Fertilizers like compost contain nutrient values like nitrogen, phosphorus, potassium and other nutrients in combined state and when decomposed it is released as the fertilizer.

Natural Inorganic: Some minerals like fluorappetite are the source of phosphate. As it is, these rocky aggregates are insoluble in water but in course of time the rock will disintegrate the minerals will liberate slowly and makes the phosphate available to plant but the release is very slow. The rock is made to react with sulfuric acid to form super phosphate which can be considered as a controlled release fertilizer.

Synthetic Fertilizers: Synthetic fertilizers are highly soluble in water and release nutrients at high rate. These fertilizers are sometimes modified to retard the release.

A.Fertilizer without any modification

B.Controlled Release Fertilizer

1.Coated controlled release fertilizer

2.Chemically modified controlled release fertilizer

3. Matrix base controlled release fertilizer.

4. Controlled release fertilizers using enzymatic inhibition.

The term controlled release fertilizer refers to the fertilizer that release nutrient to an extended period. The main objective of the study is to minimize the cost of fertilizer and to extend the period of release. Sometimes aspirations are cast to produce a fertilizer to release at a predetermined time and rate. The controlled release fertilizers could be made with several strategies but the following two are in practice.

1. Coated controlled release fertilizers: Several types of materials have been used for coating and tested for their release rates, Sulfur coated urea, neem oil coated urea and polymer coated urea are few among them. Polymers of several types as coating materials have been under study.

2. Chemically modified controlled release fertilizers: In this type release rate of fertilizer is decreased by altering the molecular structure to form a new compound. Ex: Urea formaldehyde, Isobutylidene di urea (IBDU), Crotonylidene di urea (CDU), trimethylene tetra urea oxamide, glycouril, and ammelide are some nitrogen based controlled release fertilizers. Magnesium ammonium phosphate ($MgNH_4PO_4$) is a slowly soluble source of nitrogen and phosphorous. Guanyl urea sulfate (GUS) and Guanyl urea phosphate (GUP) are readily soluble in water but are absorbed in soil colloids transforming it into mineralization and have slow release character. Among all these fertilizers sulfur coated urea is improved and favored to go for commercial production by some companies but due to the high cost its use is limited to very low percent of total production.

Application of synthetic fertilizer is highly useful in increasing the productivity. It has been in practice for some time and their benefits have been derived by the farming community. Application fertilizer in luxurious quantities has several disadvantages such as increased cost of product, root burn, loss natural resource. Loss of fertilizer may either by running water or by seepage. Excess fertilization may either cause stress to the plant or root burn. Over dosage might also lead to the condition of excess absorption and may in turn attract pest cause severe damage to crop and loss to the farmers. Therefore it is customary to use organic fertilizer to avoid this type of damage which is inherently posses slow release character. But in practice it is not possible to deliver the nutrient at a desired level by synthetic nutrients.

Therefore, a constant need/urge is felt for slow or controlled release fertilizer. The other aspects of excess usage of synthetic fertilizer are environmental degradation. The lost fertilizer may find its way either to drainage system or to underground water table. The drained water contaminates the down stream water bodies and ground water in those localities. Nitrate contamination is one such example. Application of urea or ammonia may lead to the increase in nitrate pollution in the ground water. The continued and increased usage of fertilizer may pollute ground water making the water not fit for biological consumption. The other contaminations originated from fertilizers are heavy metals such as Copper, Manganese, Molybdenum, Zinc, Iron, Aluminum, Cobalt, Cadmium, Chromium and Nickel. All the micronutrients may cause environmental degradation when applied in uncontrolled manner. All these factor demand the use of controlled release fertilizers.

IMPORTANCE OF KCL BASED CONTROLLED RELEASE AS FERTILIZER

Plant nutrient potash is normally applied as potassium chloride or muriate of potash. As potassium chloride is ionic and dissociate completely and is easily liable to loose through drainage. It is envisaged to develop potassic control release fertilizer by fixing in an inert matrix. Several inert matrixes were envisaged among them sand, fly ash, organic compost etc. In the present study sand is selected as matrix material as it is easily available to formers at no cost. The binder compatible to sand in making aggregate is cement. Though the cement is a manufactured product, it is available at low cost when compared to any other type of binders. CRF of potassium chloride is made with the procedure outlined in materials and methods. The sand matrix CRF is made and tested in the procedure outlined in chapter materials and methods. The release data are obtained in terms of concentration versus time and shown as Figure1. The figure reveals concentration of fertilizer or the leach ant increases with time. Observation of fig1 reveals three regions. The first region is initial region, where the release of fertilizer is large in short interval. It can be attributed to the fact certain quantity of fertilizer reside in large pores are transported out of the pellet. The next region which is due to increased resistance to mass transfer may be micro pore diffusion and hence decreasing mass transport conditions prevail. The third region is the one where the concentration of the fertilizer in the pore sap falls below its saturation concentration. The calculated data consisted of fraction of KCl released from the pellet (XA), rate of release of KCl& other factors.

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