Development of Flaxseed Hydrogel for NPK Encapsulation Targeting Efficient Nutrient Delivery to Plants

Eyob Sewasew Yakob

A Thesis Submitted to the Department of Chemical Engineering

School of Mechanical, Chemical, and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemical engineering (specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

June, 2024

Adama, Ethiopia

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DECLARATION

I hereby declare that this thesis entitled "**Development of Flaxseed Hydrogel for NPK Encapsulation Targeting Efficient Nutrient Delivery to Plants**" is my own work and has not been submitted to any university for similar purpose. The references used in this proposal are duly recognized by proper citations.

Eyob Sewasew	______________	______________
Name of student	Signature	Date

RECOMMENDATION

we, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled "**Development of Flaxseed Hydrogel for NPK Encapsulation Targeting Efficient Nutrient Delivery to Plants**" prepared under our guidance by EYOB SEWASEW submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical engineering (specialization in Process Engineering). Therefore, we recommend the submission of revised version of the thesis to the department following the applicable procedures.

Dr. Melaku Tesfaye Major Advisor	____________ Signature	____________ Date
Dr. Alemu Gizaw Co-advisor	____________ Signature	____________ Date

APPROVAL SHEET

We, the advisors of the thesis entitled "**Development of Flaxseed Hydrogel for NPK Encapsulation Targeting Efficient Nutrient Delivery to Plants**" and developed by EYOB SEWASEW, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Dr. Melaku Tesfaye Major Advisor	____________ Signature	____________ Date
Dr. Alemu Gizaw Co-advisor	____________ Signature	____________ Date

We, the undersigned, members of the Board of Examiners of the thesis by EYOB SEWASEW have read and evaluated the thesis entitled "**Development of Flaxseed Hydrogel for NPK Encapsulation Targeting Efficient Nutrient Delivery to plants**" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical engineering (specialization in Process Engineering).

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Dr. P. Selvakumar Internal Examiner	____________ Signature	____________ Date
Dr. Lemma Dadi External Examiner	____________ Signature	____________ Date

Final approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

____________________ Department Head	____________ Signature	____________ Date
____________________ School Dean	____________ Signature	____________ Date
____________________ Office of Postgraduate Studies, Dean	____________ Signature	____________ Date

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ABSTRACT

Agriculture plays a crucial role in sustaining human life, and the increasing demand for food production necessitates the use of fertilizers. However, chemical fertilizers pose significant environmental risks, including nutrient runoff, soil degradation, and water pollution. Moreover, the current methods of fertilizer application often result in a significant portion of the nutrients being lost or underutilized, leading to decreased agricultural efficiency. This study was able to develop a flaxseed hydrogel for NPK encapsulation. Flaxseed mucilage was extracted from flaxseed using hot water extraction method. The encapsulation of NPK solution was be carried out at temperatures of (40, 60, and 80℃*), time of (2, 3, and 4 hr), and NPK loading of (0.5, 1, and 1.5 g).citric acid was used as a crosslinker. The efficiency of encapsulation was optimized using RSM and 99.5% encapsulation efficiency was achieved at* 3.687hr, temperature at 69.14℃ and NPK loading of 1.17g. *The developed fertilizer was characterized by using XRD, FTIR, TGA, and SEM. Swelling capacity, biodegradability and also pot experiment were carried out. The developed fertilizer lasted 49 days in soil. And its water retention was higher than untreated soil. The release mechanism was found to be degradation as it is confirmed by Korsmeyer-Peppas model. The pot experiment revealed that a barley crop can last 21 days without water if the developed fertilizer is added in the soil. The results obtained from this experiment showed that the developed fertilizer can play crucial role in the agricultural sector.*

Key words: *flaxseed hydrogel, NPK encapsulation, swelling capacity, water retention, biodegradability*

LIST OF ABBREVIATIONS

CA	Citric Acid
EE	Encapsulation Efficiency
FSM	Flaxseed Mucilage
FSH	Flaxseed Hydrogel
FT-IR	Fourier-Transform Infrared Spectroscopy
NPK	Nitrogen, Phosphorus, Potassium
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SRF	Slow Releasing Fertilizer
TGA	Thermo-gravimetric Analysis
WAC	Water Absorption Capacity
WL	Weight Loss
WR	Water Retention
XRD	X-Ray Diffractometer

CHAPTER ONE

1. INTRODUCTION

1.1. Background

With the world's population steadily expanding, raising agricultural production while minimizing environmental impact is the key challenge that agriculture is currently facing (Chen et al., 2020; Stewart and Lal, 2018; Stewart and Roberts, 2012). For emerging countries with agricultural land, agriculture is important. Ethiopia's economy is primarily driven by agriculture, which also serves as the main driver of human welfare and economic progress (Elka and Laekemariam, 2020; Sisay, 2020). Over 70% of the nation's population depends on it for their livelihood (Elka and Laekemariam, 2020; Berhanu et al., 2020), and agricultural products make up the majority of the country's exports (Negash and Israel, 2017). It contributes over 37% of the nation's GDP.

Crop productivity increase is essential for promoting growth in other sectors of the economy in order to achieve food self-sufficiency (Stewart and Lal, 2018; Stewart and Roberts, 2012; Morris et al., 2007). Agriculture is therefore the primary supplier of raw materials to the beverage, textile, and food processing sectors. Expanding agricultural acreage is no longer a practical means of feeding the world's expanding population (Theriault and Smale, 2021). Thus, in order to achieve agricultural expansion, meet food needs, and ensure nutrition security, intensification measures that boost crop yield while preserving the environment are now crucial (Stewart and Lal, 2018; Theriault and Smale, 2021; Thakur et al, 2020). However, the growing usage of chemical fertilizers is crucial to agriculture (Cui, 2021). The growth of the human population affects the demand for fertilizer (Zhang, 2007).

The three main nutrients that chemical fertilizers give are potassium, phosphorus, and nitrogen (N, P, and K), which are inorganic fertilizers that are manufactured in the right amounts for different crops and growing environments. Nitrogen, or N, creates proteins and chlorophyll and encourages the growth of leaves. Phosphorus, or P, is necessary for the growth of roots, flowers, and fruits. Protein synthesis and stem and root growth are aided by potassium (K) (Mandal et al., 2009; Zhang et al., 2009). But these fertilizers cause a significant amount of nutrient waste, which is expensive for farmers and bad for the environment (Rakhimol et al., 2021). According to Trenkel (1997) and Saigusa (2000), of the synthetic fertilizers applied, about 40–70% of nitrogen, 80–90% of phosphorus, and 50–70% of potassium are lost to the environment and cannot be absorbed by plants. The urea market reached a volume of 177.21 million metric tons (Singhania, 2024). From the given data, over 86 million metric ton urea is lost. This results in significant losses of economic resources as well as extremely serious environmental pollution. Using slow-release fertilizers is one way to get around these drawbacks.

Slow release fertilizers (SRFs) has shown to have many advantages over conventional types, including a lower rate of fertilizer loss, a more sustainable way to supply nutrients, a reduction in the frequency of application, and a reduction in the possible side effects of overdosing (Trenkel, 2010). Important commercially available synthetic polymer coatings for SRF include polyolefin, polyurethane, and alkyd-resin-coated fertilizers (Trenkel, 2010). These polymers do, however, have a number of disadvantages, including their high cost and detrimental effects on the environment. According to Trenkel (2010), the usage of polymeric materials in coatings may cause an undesired buildup of plastic residues up to 50 kg/ha per year.

Significant efforts have been made to produce environmentally acceptable coating and encapsulating materials such as hydrogels to reduce soil pollution and costs. Therefore, the development of environmentally friendly and renewable resources such as SRF is necessary and urgent (Chen et al., 2018). Biopolymers such as lignin, starch, chitin, cellulose, and other polysaccharides are considered potential alternatives to synthetic polymers for SRFs and also can significantly contribute to the circular economy (Majeed et al., 2015).

One polysaccharide that can be used in SRF is flaxseed mucilage (FSM) composed of polysaccharides with numerous sugar units, which are linked together to form huge polymers with large molecules**.** Flaxseed (Linum usitatissimum L.) mucilage is one of the natural mucilage which is byproduct of the flax oil industry and occurs mainly at the outermost layer of flaxseed hulls (Liu et al., 2018). Flaxseed (Linum usitatissimum L.) contains approximately 3.0 – 15.2% mucilage (Maanvi Gupta, 2023). (FSM) contains heterogeneous polysaccharide which is composed of galacturonic acid (21.0–36.0%), xylose (19.0 – 38.0%), rhamnose (11.0–16.0%), galactose (12.0 – 16.0%), arabinose (8.0–13.0%) and glucose (4.0–6.0) (Fedeniuk and Biliaderis, 1994).

Polysaccharides in flaxseed mucilage have unique and dynamic properties like higher swelling (pH dependent) capacity than other biopolymers and swelling-de-swelling ability due to stimuli (Salama, et al., 2023). FSM is also easy to extract with only hot water extraction. It doesn't need additional chemicals before crosslinking. Hydrogel can be produced from flaxseed and it can be used as encapsulating polymeric matrix for fertilizers.

In this study, Flaxseed hydrogel is used for encapsulating a proportionated NPK fertilizer, glycerol is used as a plasticizer for the hydrogel matrix, and citric acid is proposed as a cross-linker.

1.2. Statement of the problem

Agriculture plays a crucial role in sustaining human life, and the increasing demand for food production necessitates the use of fertilizers (Cui, 2021). However, chemical fertilizers pose significant environmental risks, including nutrient runoff, soil degradation, and water pollution (Rakhimol et al., 2021). Moreover, the current methods of fertilizer application often result in a significant portion of the nutrients being lost or underutilized, leading to decreased agricultural efficiency. Therefore, farmers have to apply an extra dose of fertilizer and this costs money which affects farm economics. High levels of N fertilizers used by plants also contain carcinogenic substances such as nitrosamines, especially in plants such as lettuce and spinach that are eaten (Savci, 2014). Leaching directly affects water reserves causing problems for aquatic life by increasing nitrates and phosphate and therefore also disturbs flora and fauna (Zhang et al. 2014; Trinh et al. 2015). Previous studies showed that due to 30-60% losses of urea applied to the soil, reductions in crop yields were observed in terms of biomass growth (Anggoro 2011; Naz et al. 2014).

Several new methods have been developed to enhance urea performance within the recent past. The quick release and losses problem associated with conventional fertilizer can be mitigated by slow release or efficient delivery mechanism(s), especially, by polymer coating. The slow release of nutrients through fertilizers is considered the best way of providing a regular supply of nutrients to crops. Synthetic polymers have been used widely used for the production of SRF. However, these polymers have shown many drawbacks, such as their high prices and their negative impact on the environment. Moreover, the use of polymeric materials in coatings could lead to an undesirable accumulation of plastic residues of up to 50 kg/ha/year (Trenkel, 2010). To reduce soil pollution and price, concentrated efforts have been put into developing environmentally friendly coating materials. Thus, development of environmentally friendly and renewable sources as SRFs is necessary and urgent.

Therefore, this research aims to tackle the problem of inefficient fertilizer delivery by developing an environmentally friendly hydrogel that effectively encapsulates N-P-K fertilizer and enables slow – release capabilities. By doing so, this research seeks to contribute to sustainable agricultural practice and reduced environmental and economic impact.

1.3. Research question, hypothesis and choice of system

Research questions: the present work aims to answer the following major questions:

1. Is it possible to encapsulate NPK fertilizer in a flaxseed hydrogel matrix?
2. Can citric acid crosslink flaxseed mucilage to form a hydrogel which can encapsulate fertilizer?
3. Is it possible to synthesize a slow release fertilizer?

Based on the above research questions the choice of the systems is formed as follows:

1. Flax seed mucilage is chosen as a polysaccharide based biopolymer due to its swelling and have the ability to form gel.
2. Glycerol is chosen as a plasticizer and citric acid is chosen as a crosslinker.
3. Urea, potassium dihydrogen phosphate and potassium chloride are chosen as a major source of Nitrogen, phosphorus, and potassium, respectively.

Hypothesis: Due to the collective nutrient content and property of those raw materials, it might be possible to develop a slow releasing N-P-K fertilizer encapsulated in a flaxseed hydrogel.

1.4. Objectives of the study

1.4.1. General objective

The major objective of this research work is to develop a flaxseed hydrogel for NPK encapsulation targeting efficient nutrient delivery to plants.

1.4.2. Specific objectives

1. To synthesis a hydrogel encapsulated with NPK fertilizer.
2. To optimize the effect of time, temperature and loading ratio using Response Surface Methodology
3. To characterize the hydrogel encapsulated with NPK fertilizer
4. To examine the swelling capacity and water retention of the hydrogel
5. To examine the biodegradability of the developed hydrogel
6. To test the proto-type fertilizer on pot experiment

1.5. Significance of the Study

Soil has been subjected to severe nutrient deficiency triggered by natural and man-made factors. To solve the deficiency of nutrients, synthetic fertilizers have been used. For countries such as Ethiopia, whose over 70% of population is living based on agriculture, finding an efficient use of fertilizer is a must. Thus, the development of a slow releasing fertilizer will help the efficient use of fertilizers.

Developing the hydrogel encapsulated fertilizer has two fold merits. From economic perspective: fertilizers are usually lost due to water runoff and volatilization forcing the farmers to buy more fertilizers to account for lost fertilizers. So, producing this hydrogel encapsulated fertilizer will reduce the cost of fertilizers as well as the foreign currency paid for importing fertilizers. The other benefit is that hydrogel matrixes have a water holding capacity. Therefore, developing hydrogel for encapsulation of fertilizers will reduce the water needed for plants during irrigation farming. It is also suited for drought severed areas.

From environmental perspective: un-encapsulated (coated) fertilizers pose different types of environmental pollutions such as greenhouse gas emission due to volatilization of ammonia, and surface and ground water pollution. Therefore, developing the encapsulated fertilizer helps to reduce these environmental problems.

1.6. Scope of the study

The scope of this research was focused on the following points:

- Formulating NPK fertilizer and in situ loading (encapsulating) it in flaxseed hydrogel.
- Optimizing encapsulation efficiency by investigating the effect of time, temperature and fertilizer loading using RSM.
- Characterizing the flaxseed hydrogel encapsulated fertilizer.
- Investigating the swelling (water absorption) capacity and biodegradability of the proposed encapsulating material.
- Testing of the developed fertilizer prototype on a pot.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Background

Statistics data provided by the Agriculture Organization of the United Nations (FAO) have shown a steady increment in global consumption of agricultural fertilizer with an average of 1.3% annual growth in 2019–2023 (IFA, 2019).

On the other hand, the high demand for fertilizers is faced with the low fertilizer efficiency problem, which has implications for agricultural unsustainability. It has also been reported that a quarter of the urea applied to soil is lost to the environment owing to poor efficiency (Beig et al., 2020). At the same time, nutrient recovery by plants remains relatively low (e.g. around 50% for N) (Shaviv et al., 1993).it was also reported that about 40–70% of urea fertilizer lost to the environment results in severe pollution (Abraham and Rajasekharan Pillai, 1996).

The lack of controlling practices in nutrients and water loss is considered a global challenge for agriculture as it is confronted with crop production need (Salimi et al., 2020) Because of that, crop fertilization optimization is a critical element of all quality systems in primary production, such as integrated Production, GLOBAL Good Agriculture Practice and the Sustainable Agriculture Initiative (Sikora et al., 2020)

Slow release technology helps increase the urea fertilizer efficiency by reducing the nutrient release rate, thereby minimizing environmental pollution (Wang et al., 2021).

2.2. Development of slow releasing Fertilizers(SRF)

Many researchers have studied the development of SRFs from different perspectives at different stages of development. SRF provides nutrients by delaying the availability of SRF for plant uptake from the soil or reducing its high solubility in soil and water surfaces (Li and Chen, 2019; Li et al., 2019; Wei et al., 2020). The release rate of SRF can vary from hours to days or even months, as it is produced in a variety of ways.

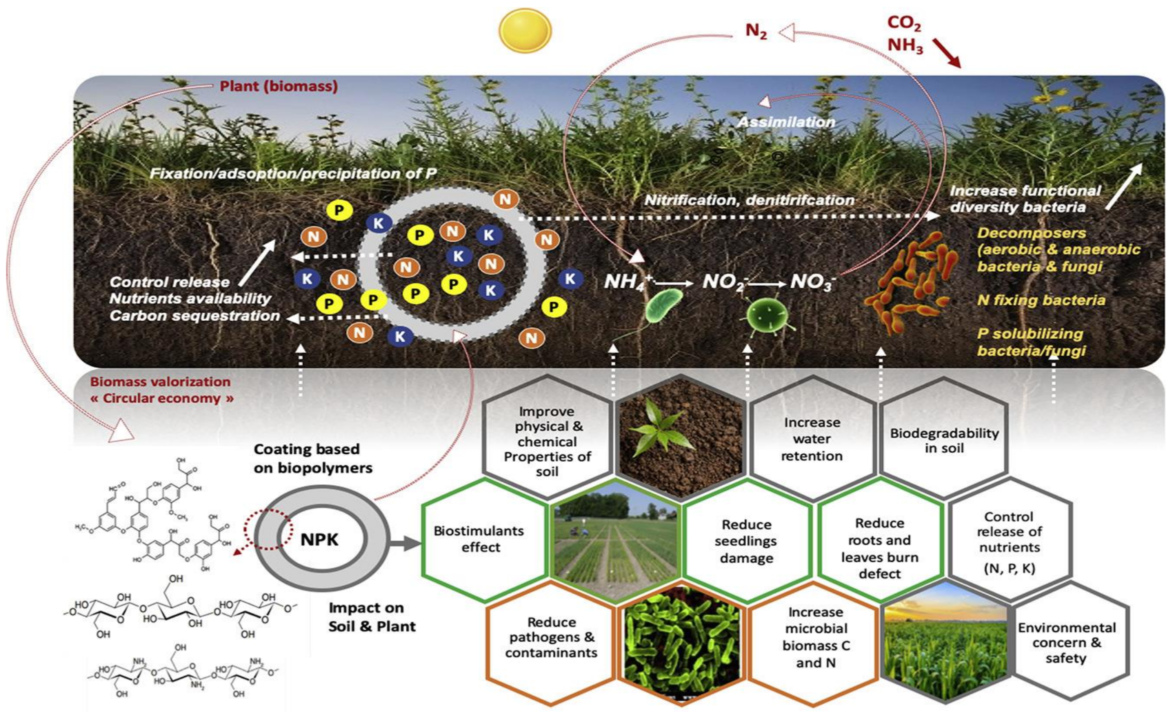


Figure 2. 2 comparison of SRFs and synthetic fertilizers (source: Fertahi et al., 2021)

2.2.1. Chemical synthesizing

One of the oldest methods to reduce the solubility of fertilizers in water is chemical synthesizing. For example, the slow-release N fertilizers were initially developed by different chemically synthesizing ways. Recently, some organic or polymers have been used to develop SRFs by forming complex or chelate compounds. SRFs can be produced in two ways. One is using organic fertilizers which are by nature uncoated slow releasing fertilizers; and they account for occupying the largest proportion of SRFs (Fan and Li, 2010). the other way is synthesizing polymers like methylene urea products through a condensation reaction of ammonium, formaldehyde, and urea at different degrees of polymerization in various molar ratios (Guo et al., 2018; Yang et al., 2016). It has, however, a limitation of low precision for synthesis.

2.2.2. Loading into porous or layer carrier

The technique of loading nutrients into inorganic materials is mainly used for the development of P-based and K-based SRFs. This is because they are reasonably stable salts. Nutrient loading can occur in either porous or layered supports although the amount of fertilizer is low (Krishnan et al., 2021; Rakhimol et al., 2021).

i. Loading into porous carrier

Zeolite-based SRFs have been developed in various technologies due to their excellent cation exchange ability and micro-porosity. Lee et al. (2013) modified natural zeolite using ammonium chloride, mono-ammonium orthophosphate, and potassium sulfate to prepare SRF. Flores et al. (2017) developed potassium release from potassium zeolite SRF extracted from coal ash. They treated the coal ash using a conventional hydrothermal process using 5mol/L KOH as the solvent and setting it at 150 °C for 24 h. Lateef et al. (2016) developed zeolite nanocomposite SRF by synthesizing nano-zeolite by coprecipitation method and impregnating it with nutrients. Zeolite nanocomposite SRF successfully slowed down the release rate.

Another material with a complex network of pores and channel structures is biochar. Biochar is a multifunctional carbon-based material known as charcoal that is produced through a pyrolysis process from waste materials such as animal waste, industrial waste, and wood residue. Due to its pore structure, large specific surface area, and functional groups such as -COO- and -O-, biochar is considered a cost-effective material and is used in agriculture (Sim et al., 2021). Using biochar as soil fertilizer improves soil properties and increases crop yields (Wang and Wang, 2019; Zhou et al. , 2021b). Zhong et al. (2018) found that combining biochar and molten urea under heterogeneous infiltration not only reduced the release rate of urea but also improved the soil environment and promoted plant growth. Jin et al. (2017) developed a slow-release biochar phosphorus fertilizer by preparing biochar SRF of different sizes from rice straw, peanut straw, and rapeseed straw under pyrolysis for 3 h at 500 °C. The slowest releasing biochar was rice straw. Similarly, Vendra Singh et al. (2020) reported that urea-loaded rice straw biochar exhibited lower release rates (91% and 98%, respectively) than urea-loaded rice husk biochar after 72 h of incubation in water. Kim et al. (2017) combined the application of biochar and SRF to reduce methane emissions and increase rice production in rice fields. Pfister and Saha (2016) also studied the effects on the growth of sunflower plants when applying commercial fertilizers based on pine and hardwood biochar.

ii. Loading into layer carriers

Due to its layered structure, clay has a large surface area and a high loading capacity that can be used for fertilizer storage. Yamamoto et al. (2016) developed Novel matrix nanocomposites using multiple steps to prepare urea matrix nanocomposites, including (1) premixing, (2) extrusion, (3) molding, and (4) curing. This system was found to have a lower release rate and a higher degree of polymerization at higher temperatures.

2.2.3. Coating

Numerous experimental studies have been conducted on SRF using different coating materials (Irfan et al., 2018). More recently, Yuan et al. (2022) investigated different oil coatings used in the development of SRFs.Materials used for coatings are generally divided into three categories: inorganic mineral compounds, such as gypsum, bentonite, and sulfur (Choi and Meisen, 1997), petroleum-based organic polymeric materials, such as polyolefins (Xu et al., 2013), polyethylene (Wei et al., 2017), polyurethane (Ni et al., 2011), polystyrene (Yang et al., 2012), superabsorbent polymer/hydrogel (Zhang et al., 2015), polyester acrylamide (Abraham and Rajasekharan Pillai, 1996), polyacetal (Chen et al., 2008), polydopamine (Majeed et al., 2016)) and natural biodegradable polymeric materials such as lignin (Majeed et al., 2017), carboxymethylcellulose (Ni et al., 2011)), starch (Chen et al., 2008) and chitosan (Majeed et al., 2015). However, Sulfur coated SRFs lowers soil pH making it difficult for crops to uptake nutrient; and also it cracks easily and have higher cost (Choi and Meisen, 1997). Whereas, Petroleum polymers are non –degradable and have higher costs.

2.2.4. Prepared with biodegradable polymers

Synthetic polymers made from non-degradable materials couldn’t be used since they do not decompose easily in the soil (Boyandin et al., 2016; Tan et al., 2017). Trenkel (2010) has reported that applying non-biodegradable coating polymers may lead to an adverse accumulation of plastic residues in soil up to 50 kg/ha/year.

The nature-inspired synthetic biodegradable polymers such as polylactic acid, polyvinyl alcohol, poly-dopamine, and derived from natural resources like poly(3-hydroxybutyrate), are now widely accepted as biopolymers and used in developing various polymer coating (PC)-

SRFs although they have higher cost and long biodegradation time (Costa et al., 2013; Jia et al., 2013).

Raw natural biodegradable materials, such as starch, cellulose, lignin, chitin, and other polysaccharides (e.g., k-carrageenan) or proteins, cannot be used as effectively coating material in pure natural form due to their inherent properties. Various chemical and physical modifications have been developed to overcome these weaknesses to improve their performances (Bao et al., 2015, 2019, 2018). The biodegradable coatings that consist of modified starches (Naz and Sulaiman, 2016), cellulose (El Assimi et al., 2021; Kassem et al., 2022), and lignin (Lu et al., 2022; Mulder et al., 2011) have been developed.

The use of biodegradable materials will reduce the negative environmental impacts associated with conventional polymers, but it has to be demonstrated that they indeed completely degrade either in the environment or during composting (Sintim et al., 2019; Sintim and Flury, 2017).

2.2.5. Hydrogel-based systems

It is anticipated that hydrogels can effectively load nutrients through physicochemical interactions and prevent nutrient release before biodegradation. In agricultural and horticultural applications, hydrogels enable process economy by reducing water consumption and irrigation frequency, particularly in drought-prone areas

Some of the advantages of hydrogels for producing SRFs include improving soil through aeration, mitigating soil degradation, reducing water evaporation losses, controlling environmental pollution, reducing plant mortality, and extending nutrient retention in soil. hydrogels can be prepared from hydrophilic polymers in which the polymer chains cross-linked by physical entanglement and chemical grafting form a three-dimensional structure that allows them to absorb and retain a large amount of water even under external pressure (Wang et al., 2012; Xie et al., 2011;).

Hydrogels can be divided into natural, synthetic, and synthetic-natural polymers, depending on their material resources. Natural polysaccharides (such as starch, cellulose, chitosan, alginate, and their derivatives) and polypeptide based (such as gelatin, collagen, and soy isolate protein) are well-known biomaterials from renewable resources, which can be used to develop environmentally friendly hydrogels.

Most of natural polysaccharides are extracted from the biomass in many stages. i) extraction using either a solvent or a chemical catalyst, ii) filtration and washing, iii) purification, and iv) drying. Another very important parameter is the availability of biomass (algal, wood, etc.) and the competition with other sectors (food/feed, cosmetic). It would therefore be necessary to develop new organic coating based on biopolymers, more reliable, renewable, and not competitive with another industry, less expensive and non-polluting chemical modifications. Due to its functional properties such as its swelling and water retention capacity, low cost, and wide sources, flaxseed has a good potential for preparing slow release fertilizers.

Numerous ways of loading fertilizer into hydrogels have been tried and developed. They are classified as coated and matrix types. For example, Ahmed Khan et al. (2019) reported a coating process that first sieved the (Nitrogen, Phosphorus, and Potassium) NPK fertilizers to particle sizes below 2 mm. The starch was then added to NPK fertilizers as a binder to ensure the NPK granules were uniformly coated with the hydrogel fabricated by suspension polymerization. The specific process was to mix 10 g of starch with 5 g of NPK in a beaker with continuously sprayed distilled water (about 10–15 mL) until NPK fertilizer was coated entirely with starch. The beaker was constantly rotated to ensure that it was evenly distributed over the NPK and starch, which helped to prevent the starch from clumping. Then, the starch-coated NPK was placed on a sieve to remove excess starch before being coated with hydrogel. 5 g of SAP was put into a petri dish for the final coating process, then rolling the starch-coated NPK fertilizer until they were completely covered. Finally, the hydrogel-coated NPK fertilizers were dried at 105 ℃ for 24 hr. and then stored in a desiccator before characterization. One of the polysaccharides that can be used to produce a hydrogel loaded with fertilizer is Flaxseed.

2.3. Preparation of hydrogel from flaxseed

Flax is one of the oldest crops and its seeds (flaxseeds/linseeds) are the rich source of carbohydrates (Barbary et al., 2009; Kaewmanee et al., 2014). Many studies were carried out on the preparation, composition, characteristics, and application of flaxseed hydrogel. It can be produced by hot water extraction (Haseeb et al., 2018), Karami et al. Flaxseed hydrogels were prepared by hot water extraction, and the results showed that polysaccharide hydrogels extracted from different flaxseed varieties had significant differences in chemical composition and functional properties. All hydrogel samples had presence of high proteinaceous components in them which, contributed to their foaming and rheological properties.

2.4. Modification of flaxseed hydrogel

Polysaccharide derived hydrogels are more preferable for use than synthetic hydrogels. Since, they are biodegradable, and they play important role in biosafety and sustainability. However, they have their own limitations such as: uncontrolled hydration, pH dependent solubility, thickening, and drop in viscosity during storage (Rana et al., 2011). Many researchers use different methods such as cross-linking, esterification, fillers dispersion and blending to modify the property of the hydrogel.

2.4.1. Crosslinking

Polysaccharide derived hydrogels can be altered by using cross linkers. The properties of cross-linked gum derivatives depend mainly on cross-linking density (the ratio of moles of crosslinking agent to moles of polymer repeating units). Crosslinking of gums requires availability of active functional groups, including free alcohols, carboxylic acids, polyacrylamide, and phosphate. Chen et al (2006) studied on how dissolution temperature, pH value, addition of differential valence mineral salts affected the gel strength of flaxseed gum. According to Chen et al different salts had different effects on the gel strength. Initial addition of NaCl resulted in reduction of the gel strength, which attributed to compression of the double electric layer of molecules. While addition of $CaCl_2$ up to 0.3% resulted in increase of gel strength and the converse was obtained above 0.3%. As the Zeta potential was lowered, the intramolecular charge repulsions decreased progressively. The polysaccharide molecules were contracted and the junction zone numbers were decreased due to the addition of monovalent and divalent cations (Mazza & Biliaderis, 1989).

2.4.2. Esterification

Esterification protocols such as acetylation (Teramoto, et al., 2006), succinylation (Fang, et al., 2000), sulfation (Abatangelo, et al., 1997), and tosylation (Gericke et al., 2012) can be used to modify Polysaccharide gum structures.

2.4.3. Blending

A polymer blend is a physical mixture of two or more polymers with no chemistry bonding between them.de Paiva et al. observed that Mixing flaxseed mucilage with polyvinyl alcohol (PVA)significantly influenced the thermal stability but did not change water vapor barrier properties compared with pure mucilage films and pure PVA films. According to de Paiva et al. (2020), these films made from blends of flaxseed and PVA mucilage extracts may offer an intriguing and beneficial substitute for creating bio-based packaging for various uses.

2.5. Application of flaxseed hydrogel in developing SRFs

Flaxseed hydrogel can be used in the production of slow releasing fertilizers. The fertilizers can be encapsulated in the gel matrix and form a slow release fertilizer. Until now there is no research on formulating and embedding NPK fertilizers in flaxseed hydrogel matrix. Therefore, the aim of this study was to formulate a biodegradable NPK fertilizer and encapsulate it with flaxseed hydrogel for slow release.

CHAPTER THREE

3. METHODOLOGY

3.1. Materials, chemicals and reagents

Soil was collected from a farm land in Adama city, and Flaxseed was purchased from local market in the city. The major materials that were used for performing various experimental works in this study are pH meter, Analytical balance, heating mantle and magnetic stirrer, beaker, Beakers, Measuring Cylinders, Conical Flasks, Funnels, Petri Dishes, Centrifuge Tubes, Samples Holder, Centrifuge, Sieves, Poly-mixer, air tight container, Pots, and oven. For analysis purposes, X-Ray Diffraction (XRD), Thermo-gravimetric analysis (TGA) Differential Scanning Calorimeter (DSC) and Fourier-Transform Infrared Spectroscopy (FT-IR) have been used.

Chemicals used in this research are citric acid, glycerol, potassium chloride (KCl), Urea, potassium dihydrogen phosphate (KH_2PO_4), Glycerol (99%), sodium acetate, acetic acid, HCl, boric acid, sodium borate and distilled water were used for different stages of this study. All the chemicals, reagents, and equipment used to carry out various procedures and characterize the samples were analytical grade and standard Laboratory tools.

3.2. Methodology

3.2.1. Preparation of proposed grade fertilizer

There are many types of commercial fertilizers that consist of mixing the substances containing nitrogen (N), phosphorus (P) and potassium (K) in different proportions. In this study, the sources of N, P and K used were urea, potassium dihydrogen phosphate, and potassium chloride, respectively. These materials were grounded and mixed at 5000rpm in a ratio of 20:20:20 ratio of N, P_2O_5, and K_2O, respectively.

The urea contains 46% nitrogen, KH_2PO_4 contains 52% P_2O_5 and 34% K_2O, and KCl contains 62% K_2O. therefore, 45 gram of urea, 40 gram of KH_2PO_4 and 11 gram of KCl were used to prepare a 96 gram NPK (1:1:1) fertilizer. The fertilizer was then sieved using 1mm sieve and stored in an air tight container.

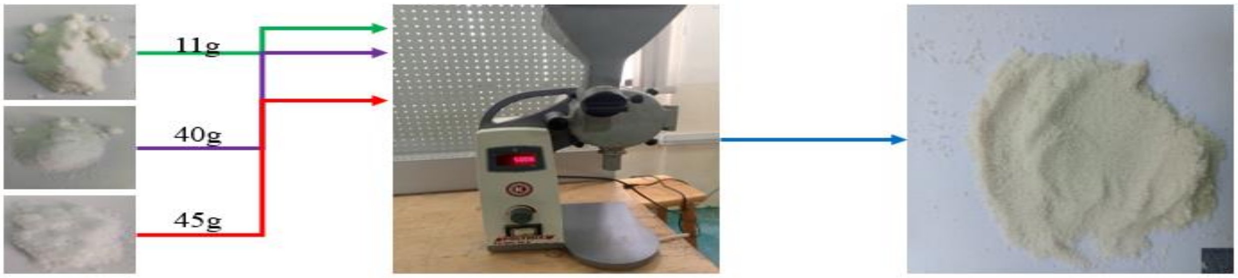


Figure 3. 2 preparation of NPK fertilizer

3.2.2. Flaxseed mucilage extraction

Flaxseed mucilage was extracted using the hot water extraction method. As reported by Maanvi Gupta (2023), 100g of flax seeds were soaked in 800ml of distilled water for 12 hrs. Then, heated up to 80℃ by using heating mantle coupled with magnetic stirrer for 30 minutes. The filtrate was filtered through the muslin cloth. Precipitated mucilage was then spread on petri dish and dried in hot air oven at 50℃ for 24 hours. Dried mucilage was then grinded using mortar and pestle ass illustrated in figure 3.2.

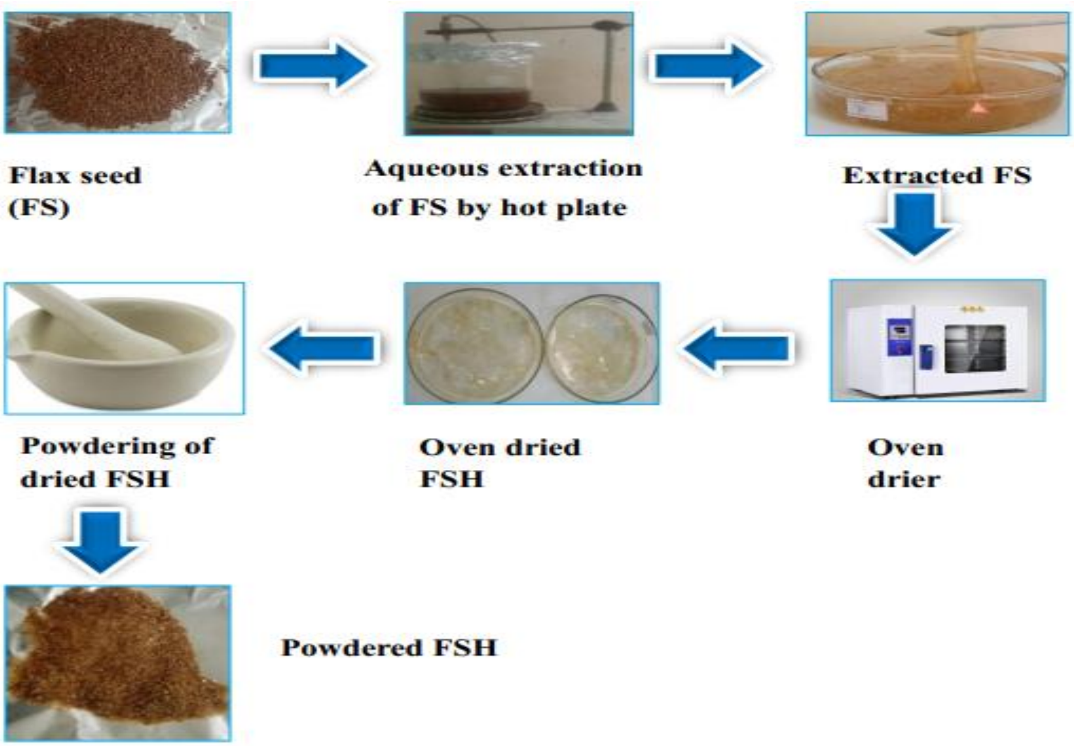


Figure 3.2. Hot water extraction of flaxseed mucilage

3.3. In Situ preparation of fertilizer loaded flaxseed hydrogel (FSH).

The prepared fertilizer was mixed using magnetic stirrer with 100 ml distilled water in a beaker. Then, 2wt% of dried flaxseed mucilage was added into the solution. The mixture was then heated to 40, 60, and 70°C for 2, 3, and 4hr. the fertilizer was also varied with the ratio of dried mucilage to fertilizer 2:1, 1:1, and 2:3. These three factors values were determined from a preliminary experiment**.** Then 5wt% glycerol and 15wt% citric acid were added and continuously stirred for 5 minutes. The mixture was stirred for 30 minutes without heating for good homogeneity. The solution was then poured on petri dish and oven dried at 50C. Finally, the cross-linking was carried out 80C for 2hrs as per the preliminary research done by the author of this thesis.

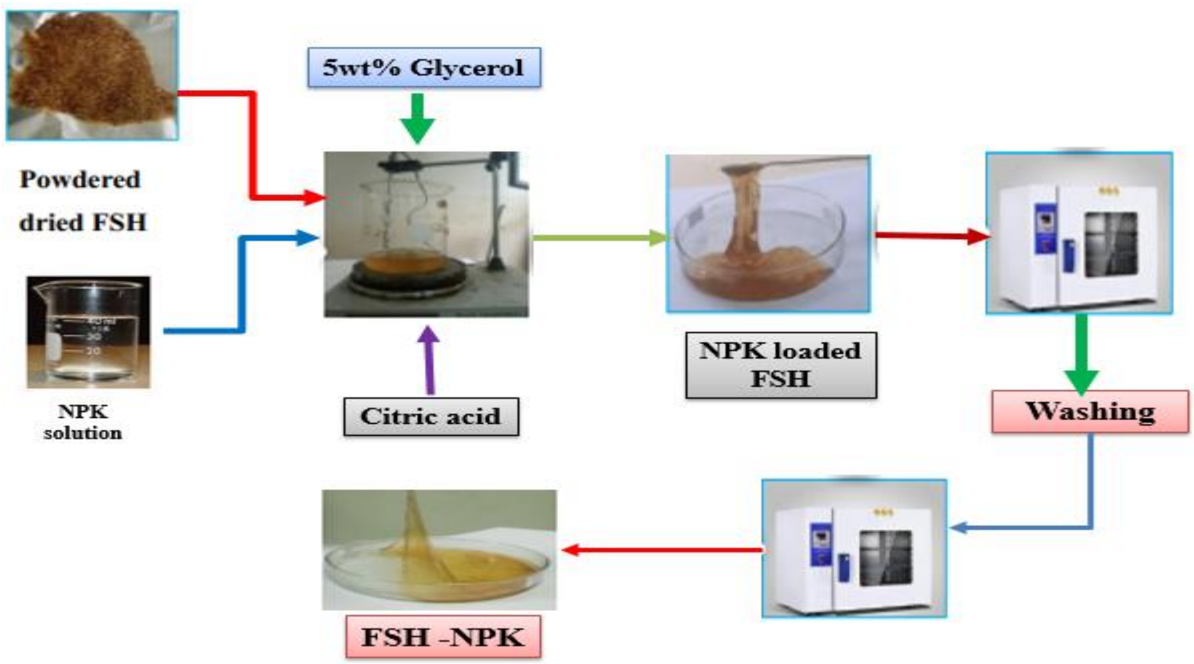


Figure 3.3. In situ preparation of NPK loaded flaxseed mucilage

3.3.1. Optimization of the encapsulation (loading) efficiency.

Encapsulation (loading) efficiency was optimized by response surface method (RSM) using Design Expert 13.0.0.5 software. It was optimized by a three-level factorial Box–Behnken experimental design; 17 experimental runs were applied. But before using RSM one parameter at a time was investigated to select the upper and lower bounds. The upper and lower bounds of the parameters were selected as shown in the table below.

Table 3.1. Box Behnken experimental design matrix

Name	Units	Low	High
Temperature	C	40	80
Mixing time	Hr	2	4
Loading (NPK/1g FSM)	G	0.5	1.5

Table 3.2. Summary of experimental design of Box- Behnken

Run	Factor 1	Factor 2	Factor 3	Response 1
	A: Temperature	B: Time	C: Fertilizer load	Loading efficiency
	C	hr	G	%
1	40	3	1.5	
2	60	3	1	
3	80	3	1.5	
4	40	3	0.5	
5	80	3	0.5	
6	60	2	1.5	
7	60	3	1	
8	40	4	1	
9	80	2	1	
10	60	4	1.5	
11	60	3	1	
12	60	2	0.5	
13	60	4	0.5	
14	40	2	1	
15	60	3	1	
16	60	3	1	
17	80	4	1	

Analysis of variance (ANOVA) was used to analyze the result and model the response variable, and to check the significance of the fitted model. The encapsulation efficiency was analyzed by determining the masses of N, P, and K using Kjeldhal's method, Olsen method, and flame photometer, respectively.

Finally, the encapsulation of NPK was calculated by subtracting the amount of the unencapsulated fertilizer from the total amount of fertilizer prepared as shown in equation 3.1 (Olivares et al., 2018).

$$\text{EE (\%)} = \frac{\textit{the amount of fertilizer loaded}}{\textit{the amount of fertilizer prepared}} \times 100\% \qquad \text{……… Equation 3.1}$$

3.4. Characterization

FT-IR Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was used for the investigation of the characteristic functional groups of FSM, FSH, and FSH-NPK. 10 mg of each sample were used. The FT-IR spectra was recorded by using FT-IR spectrophotometer in in the range of 4000 to 500 cm^{-1}.

X-Ray Diffraction (XRD)

X-ray diffraction is a powerful technique that helps to identify the structure, phase purity, degree of crystallinity and unit cell parameters of a given sample (Arya et al., 2019). The XRD patterns are recorded by the measurements of the angles at which the X-ray beams are diffracted by the periodicity of the sample.

Scanning Electron Microscope (SEM)

SEM is a type of versatile electron microscope, due to its several characteristics, is commonly used to investigate the surface structure (polished or rough) or subsurface sample with relatively large dimensions. 10mg of each samples (FSH and FSH-NPK) was used to study the surface morphology.

3.5. Swelling Capacity tests

The hydrogel and FSH –NPK were dried in an oven at 50℃ for 24 h and stored in a desiccator. Then, FSH and FSH-NPKs (with a load of 0.5 gram, 1 gram and 1.5 gram) were immersed in distilled water within separate beakers for 24 hours. After removing excess water and drying the swollen samples at room temperature for 10 min, then it was weighted. The water absorption (WA) was calculated according to Equation 3.2 (Wang et al., 2012).

$$WAC\ (g/g) = \frac{M1 - M2}{M2} \times 100\% \qquad \text{....... Equation 3.2}$$

Where, M1 and M2 refer to the weight of the swollen and dried absorbent material, respectively.

3.6. Soil burial test

3.6.1. Collection of soil

Soil was collected from a farm land in Adama city, Ethiopia using grid sampling method as per the request of Batu Soil Research Center**.** Then, the soil samples were sent to study the amount of nutrient is available.

3.6.2. Microbial degradation using weight lose test

To evaluate the biodegradability of the flaxseed hydrogel was conducted for 49 days. The hydrogel was weighed and wrapped with stainless steel wire mesh in order to minimize the loss of the hydrogel fragments during soil burial process. The hydrogel was buried approximately 5cm beneath the surface of the soil and the soil was maintained at 30 wt% of water holding capacity by weighing and adding water if necessary throughout the test (Phang et al., 2011)**.**

The hydrogel was transferred out from the soil at different time intervals (3, 7, 14, 21, 28, 35, 42, 49 days). Then, the hydrogel was put in an oven at 60℃ overnight after washed to remove all the debris and plankton microorganisms. The weight of dried hydrogel was measured. The weight loss was determined using the equation (Wang et al., 2012):

$$WL\ (\%) = \frac{Mo - M1}{Mo} \times 100\%$$ ……. Equation 3.3

Where WL% is weight loss in percentage, m_o is the initial mass and m_t is the final mass. An average of three measurements will be taken.

3.6.3. Rate of release of fertilizer in soil

To study the release behavior of fertilizer, encapsulated hydrogel was buried in soil samples. The samples were kept in a plastic bottles and were properly covered and incubated for different periods at room temperature. Throughout the test, the sample soils were maintained at 30wt% of water holding capacity by weighing and adding water if necessary. After 3, 7, 14, 21, 28, 35, 42, and 49 days of incubation periods, the remaining of encapsulated hydrogel was removed from the sample soil and was washed with distilled water to remove all debris and plankton microorganism and then was dried at room temperature overnight to estimate the contents of N, P, and K using Kjeldhal's method, Olsen's method and flame photometer, respectively.

3.6.4. Measurement of Water Retention in Soil

Fertilizer-imbedded hydrogel (5 gram) was grounded and well mixed with dry soil (below 2mm in diameter) and kept in a cup and tap water was added slowly into the cup and weighed (W1). A controlled experiment, i.e., without fertilizer-imbedded hydrogel (plain soil sample), was also carried out. The cups were maintained at room temperature and weighed every 5 days (Wi) over a period of 20 days. The water retention percentage (WR %) of soil was determined using the following equation (Wu and Liu, 2008) :

$$WR\ (\%) = \frac{Wi}{Wo} \times 100\%$$ ……. Equation 3.4

3.6.5. Pot test

The fertilizer encapsulated hydrogel was tested on pot. 3 pots with similar soil and barley seed were prepared. Then on the first pot, the developed hydrogel was added. On the second pot, a commercial fertilizer (NPK) was added. Then, on the third pot there was no fertilizer; it will be the controlled sample. The three pots were placed at the same place and were provided with the same watering. The height and leaf number of the crop were measured and analyzed.

a b c

Figure 3.4 pot experiment a) control b) commercial NPK-loaded and c) FSH-NPK loaded

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1. Yield of the FSM extraction

From the preliminary experiment, a maximum of 14.1% of mucilage was extracted from 100g of flaxseed soaked in 800ml for 12 hours heated with 80℃ for 30min with a magnetic stirrer.

4.2. Design experiment result of FSH-NPK

Table: 4.1 design experiment results

Run	Factor 1 A: temperature ℃	Factor 2 B: time hr	Factor 3 C: fertilizer load g	Response 1 Loading efficiency %	Total NPK Loaded g
1	40	3	1.5	48.5	0.728
2	60	3	1	97.1	0.971
3	80	3	1.5	85.8	1.287
4	40	3	0.5	60.2	0.301
5	80	3	0.5	98.7	0.494
6	60	2	1.5	84.5	1.268
7	60	3	1	97.2	0.972
8	40	4	1	54.2	0.542
9	80	2	1	94.2	0.942
10	60	4	1.5	88.7	1.331
11	60	3	1	97.3	0.973
12	60	2	0.5	99	0.495
13	60	4	0.5	98.5	0.493
14	40	2	1	53.8	0.538
15	60	3	1	97.2	0.972
16	60	3	1	97.3	0.973
17	80	4	1	96.5	0.965

Table 4.2. ANOVA result on encapsulation efficiency

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5406.53	9	600.73	788.25	< 0.0001	significant
A-temperature	3140.28	1	3140.28	3594.47	< 0.0001	
B-time	5.12	1	5.12	5.86	0.0460	
C-fertilizer load	298.90	1	298.90	342.13	< 0.0001	
AB	0.9025	1	0.9025	1.03	0.3433	
AC	0.3600	1	0.3600	0.4121	0.5414	
BC	5.52	1	5.52	6.32	0.0401	
A^2	1849.78	1	1849.78	2117.31	< 0.0001	
B^2	10.58	1	10.58	12.11	0.0103	
C^2	36.89	1	36.89	42.23	0.0003	
Residual	6.12	7	0.8736			
Lack of Fit	6.09	3	2.03	0.2544	< 0.856	
Pure Error	0.0280	4	0.0070			
Cor Total	5412.64	16				

From the ANOVA (Analysis of Variance) Table, 4.2 results the higher F-Value and the lower P-value (<0.0001) indicate significance for the regression model. As the result demonstrates the model, the F-value of 788.25 implies it is insignificant. There is only a 0.01% chance that an F-value this large could occur due to noise. The p-value less than 0.05 imply that the model is statistically significant.

Table 4.2 gives clarity on interaction of the independent variables which is extremely important. The result showed that temperature (factor A) and water volume (Factor C) are the major important variable with P-value < 0.0001, and < 0.0001 respectively. Time is also important, although it has lesser significance compared to the other two factors with P-value 0.0460. In addition to that, interaction effect of BC (time and NPK loading) affects the loading efficiency, and From the second polynomial model, A^2, B^2 , and C^2 are with P-values < 0.0001, 0.0103, and 0.0003. The Lack of Fit of the F-value 0.2544 implies the Lack of Fit is not significant relative to the pure error.

$$Y = 97.1 + 19.81A + 0.8B - 6.11C + 0.475AB - 0.30AC + 1.17BC - 20.96A^2 - 1.58B^2 - 2.96C^2$$

4.2.1. Model Adequacy

The regression model was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared, and predicted R-Squared having a value 0.9989, 0.9974, and 0.9820, respectively as shown from table 4.3. The goodness fitness of the model was measured by a coefficient of determination R^2, which measured how well the real experimental data points have been approximated together with the regression model. As the result in a table, 4.3 expressed the value of $R^2 = 0.9989$ indicates the better fit of experimental data to that of predicted one. The value of larger Regression coefficient (R^2) approach to 1 illustrates, the validity of model in which it implies an acceptable agreement among the actual and predicted data. The Predicted R^2 of 0.9820 is in reasonable agreement with the Adjusted R^2 of 0.9977; i.e. the difference is less than 0.2. Therefore, this demonstrates that the measured data very well fitted with a quadratic model of the predicted value.

Table 4.3 the model adequacy measures

Std. Dev.	**0.9347**	R^2	**0.9989**
Mean	85.22	**Adjusted R^2**	0.9974
C.V. %	1.10	**Predicted R^2**	0.9820
		Adeq Precision	72.3280

4.2.2. Optimization of the responses

The response optimization was used to identify the combination of independent variables particularly temperature, time, and fertilizer loading with response of encapsulation efficiency. The goal of the process was to obtain maximum encapsulation within the range of 1 gram to

1.5gram fertilizer loading. According to the result obtained from optimizer Design-Expert version 13 software the maximum encapsulation of NPK (99.5%) was achieved by using time at 3.687hr, temperature at 69.14℃ and NPK loading of 1.17g.

The validation experiment showed that 95.2% of NPK fertilizer was encapsulated using the optimized parameters.

4.2.3. Plots of interaction effects

To analyze the combined effect of the independent variables on the encapsulation efficiency of NPK in FSH, graphical representation of two-dimensional 2-D and three-dimensional 3-D surface plots were employed on (Fig.4.1, 4.2, 4.3).

RSM (BBD) analysis on figure 4.1 revealed that encapsulated efficiency increase with increase in temperature and time. Maximum encapsulation efficiency was observed around 60 ℃ and 2 hrs. But, the encapsulation efficiency started to decrease with increasing in temperature. The reduction in encapsulation efficiency can be attributed to the loss of gelation of FSM.

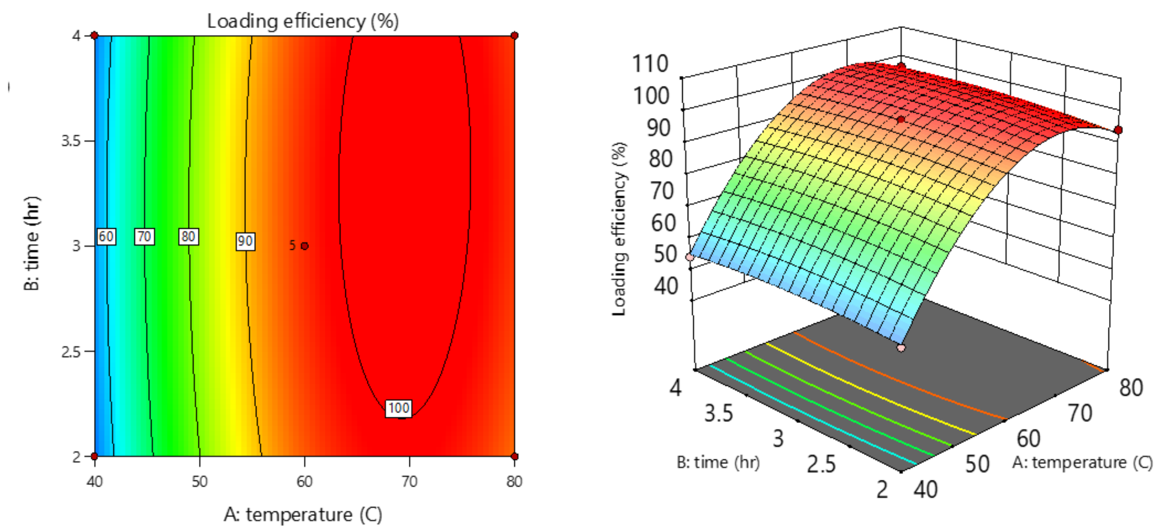


Figure 4.1. Contour and 3-D plot for effect of temperature and time on the efficiency of encapsulation

Figure 4.2 shows that increasing the temperature has a positive effect on the efficiency of encapsulation. But, the increase in loading of NPK decreased the efficiency. This can be explained as the saturation of fertilizer reached in the hydrogel matrix.

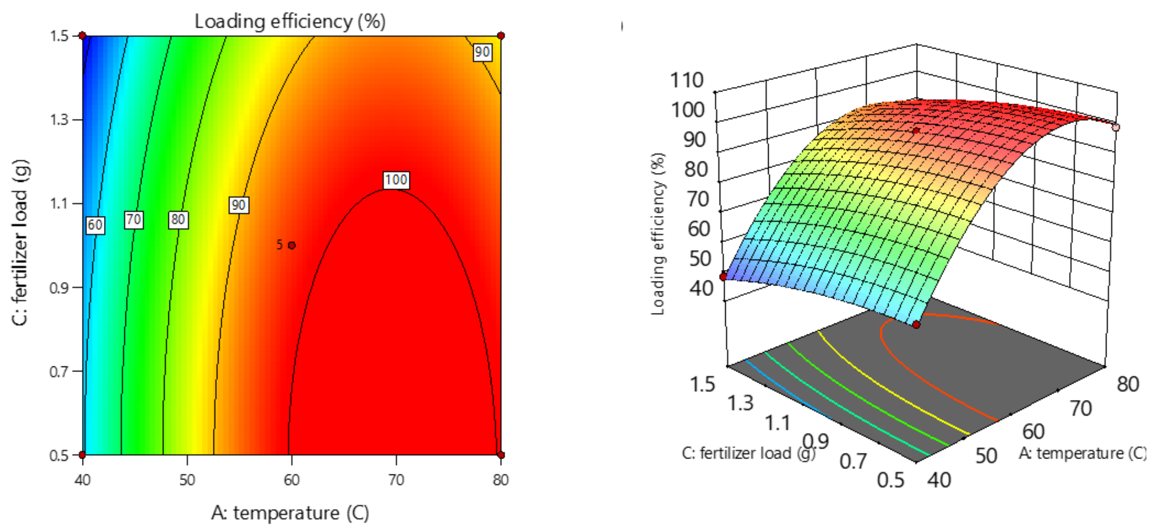


Figure 4.2. Contour and 3-D plot for effect of temperature and NPK loading on the efficiency of encapsulation

Figure 4.3 shows that fertilizer loading efficiency increases with simultaneous increase of NPK loading and increase of time. This can be explained as the NPK gets time to int9eract and being encapsulated in the hydrogel matrix, more fertilizer can be encapsulated.

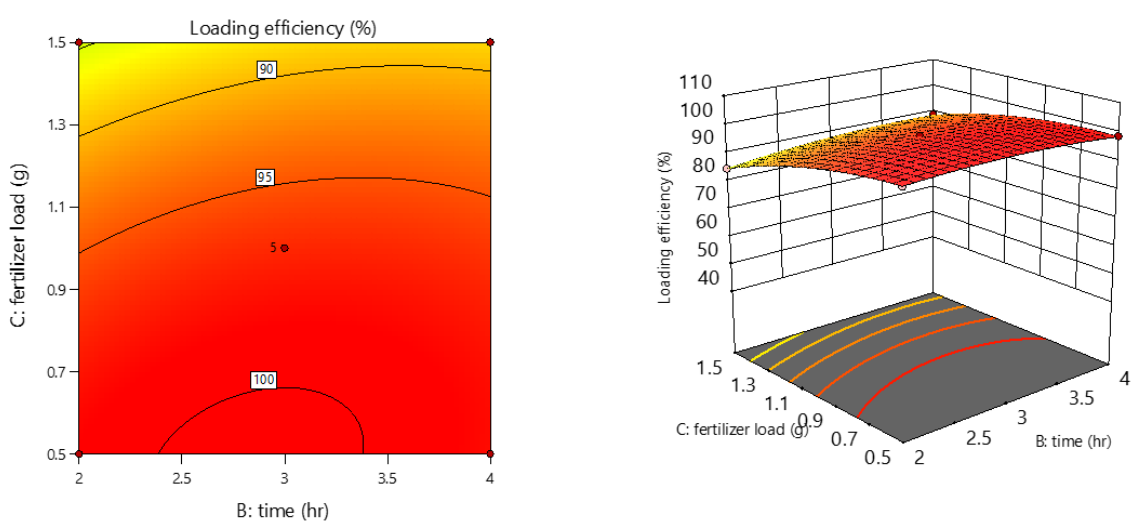


Figure 4.3. Contour and 3-D plot for effect of temperature and NPK loading on the efficiency of encapsulation.

4.3. Characterization

4.3.1. FTIR Spectroscopy

In order to ascertain the crosslinking mechanism and to illustrate the functional groups of flaxseed mucilage (FSM) and flaxseed hydrogel (FSH), FTIR was used. Figure 4.4 shows the FT-IR of FSM and FSH. At 3255 cm^{-1}, FSM showed a stretching mode of –OH groups which can be related to sugars (rhamnose and xylose) or phenolic compounds of mucilage (Bhatia and Lohan, 2019; Safdar et al., 2020). Flaxseed mucilage (FSM) showed characteristic peaks at 2927 cm^{-1}, related to the C-H bonds of the CH_2-CH_3 (alkane) groups (Bhatia and Lohan, 2019) and to the symmetric stretching vibrations of carboxylic acids associated with saturated –CH bonds (symmetric and asymmetric mode) due to free sugar (Safdar et al., 2020). At 1593 cm^{-1}, FSM showed a peak to the C=O bonds asymmetric stretching vibration of the Amide I which has covered C=O elongation of galacturonic acid groups and also attributed to carboxyl group indicating the presence of uronic acid (Bhatia and Lohan, 2019). At 1407 cm^{-1}, a characteristic peak to C-OH bond associated with uronic acid and due to –CH bending and also the presence of carboxyl groups and C-C vibrations was showed (Bhatia and Lohan, 2019). At 1028 cm^{-1}, a characteristic peak associated with the C-O link present in guluronic acid, mannuronic acid and pyranose (Hadad and Goli, 2018; Safdar et al., 2020). Moreover, C-O-C stretching band which has the polysaccharide backbone characteristic.

On the other hand, FSH showed similar peaks except for three peaks at 1713 cm^{-1}, 1211 cm^{-1}, and 1110 cm^{-1} which are related to the "rule of three" (Smith, 1999). All esters give three strong infrared bands that appear around 1700 cm^{-1}, 120 cm^{-1} 0, and 1100 cm^{-1}. This pattern of bands is diagnostic for esters, and is called the "rule of three". The first is due to C=O stretch of the ester group (Smith, 1999). The second rule is due to asymmetric stretching of the C-C (vibrational) and C-O bonds attached to the carbonyl carbon and it is called the "C-C-O" stretch (Smith, 1999). The third of the rule of three bands, which appears around 1100 cm^{-1}, is due to a vibration involving the ester oxygen and the next two carbons in the hydrocarbon chain attached to it. In this vibration, the O-C and C-O bonds stretch asymmetrically (Smith, 1999). This vibration is called the O-C-C stretch. These three peaks indicate that crosslinking is carried out due to the esterification of –OH groups with citric acid.

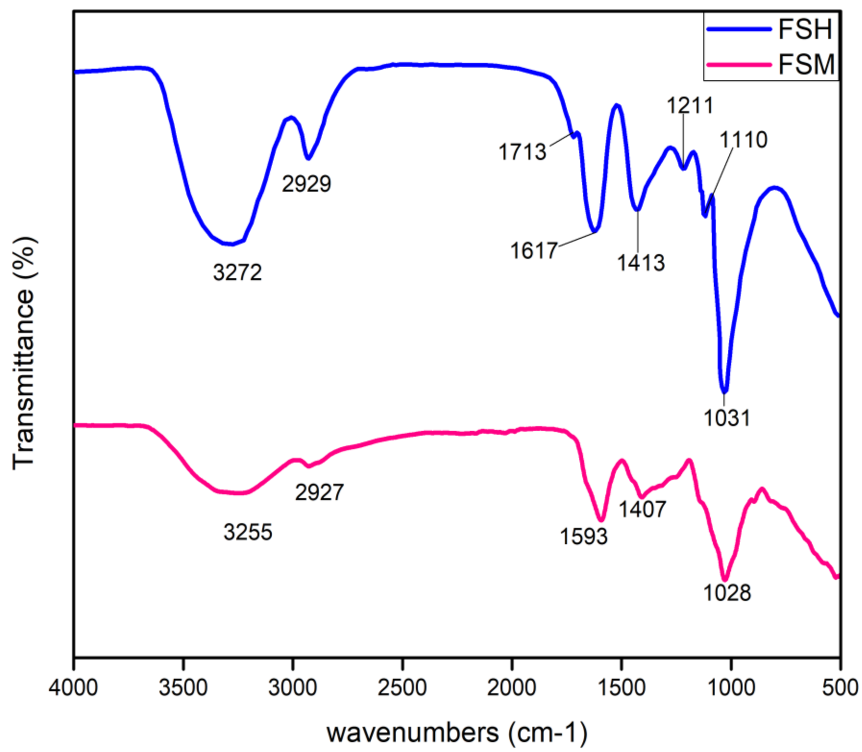


Figure 4.4. FTIR plot of FSM and FSH

FT-IR of FSH-NPK is shown in figure 4.5. Apart from increasing in intensity around 3315cm^{-1} due to the addition of urea. This band is characteristics of -OH bonds and N-H groups. 2932 cm^{-1} asymmetric stretching and 2880 cm^{-1} symmetric stretching of C-H bonds of alkanes. C-O bond of urea is also shown at 1659 cm$^{-1.}$ At 1627cm^{-1} C=O and N-H bonds have peaks. C-N bond have peaks at 1467 cm^{-1} and 992 cm^{-1}. Phosphates are detected around 920 cm^{-1}. Other peaks are similar to the FTIR of FSM and FSH with a shift in peak. For instance, C-H bonds shifted to 2932 cm^{-1} and additional peak was formed around 2880 cm^{-1} which can be the asymmetric stretching of C-H bonds.

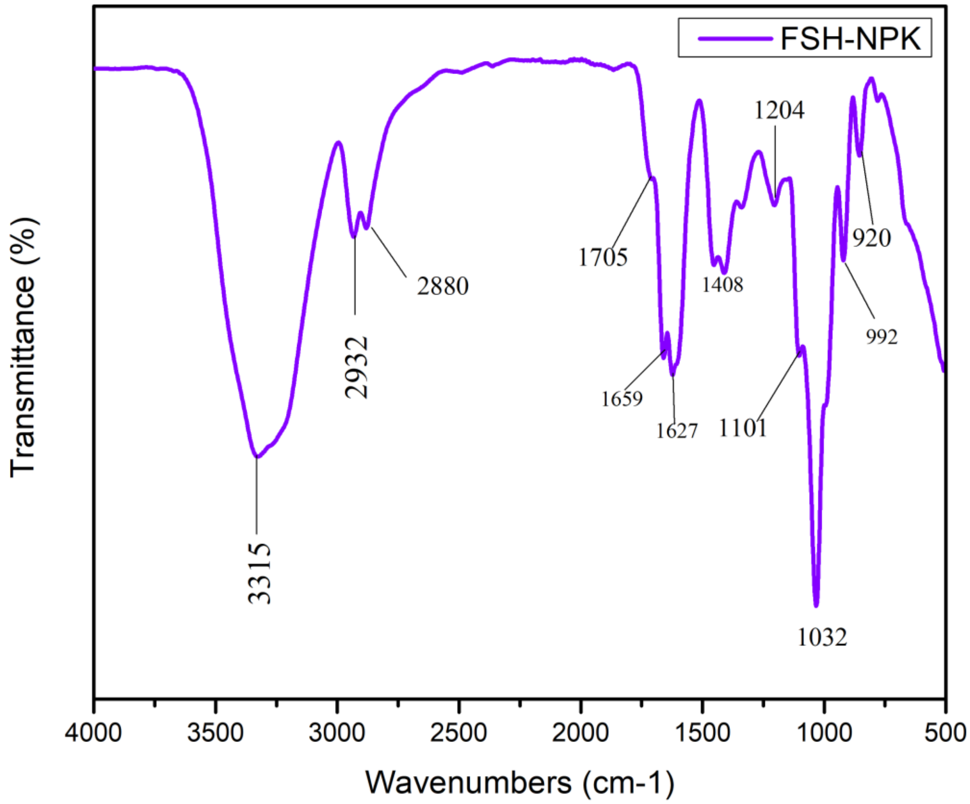
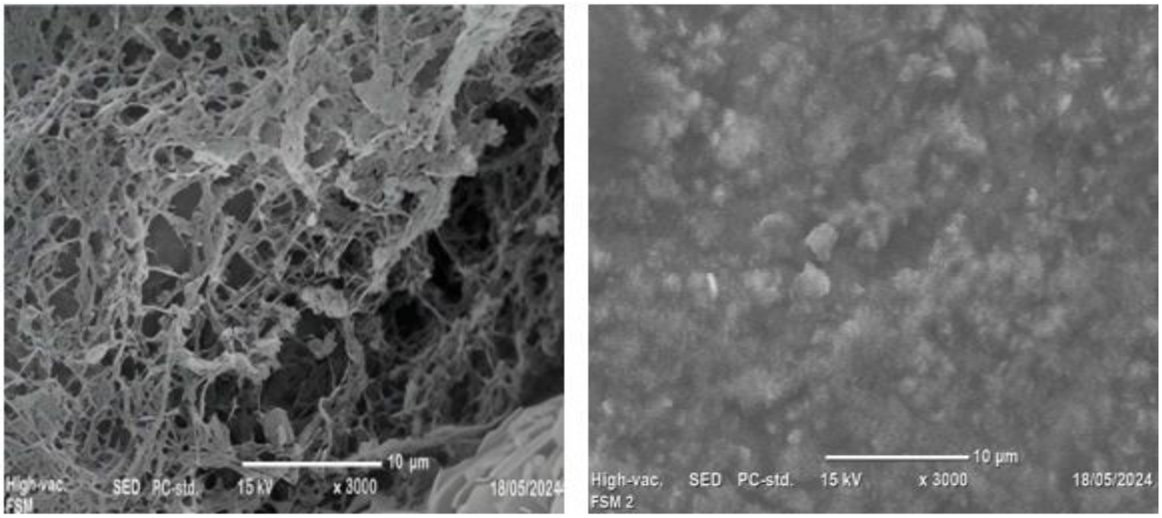


Figure 5.5. FTIR plot of FSH-NPK

4.3.2. Scanning Electron Microscope

The surface morphology examined using scanning electron microscope SEM showed that the flaxseed hydrogel (FSH) has a porous like 3-D structure which can be attributed to the crosslinking of FSM with citric acid. Whereas, the SEM image of FSH-NPK showed that the hydrogel's free spaces are occupied by the loaded NPK fertilizer.



a) b)

Figure 4.6 SEM images of FSH (a) and FSH-NPK (b)

4.3.3. Thermo-gravimetric Analysis

TGA studies were done to examine the thermal stability of FSM, NPK, and FSH-NPK. The TGA thermograms for flaxseed mucilage, NPK fertilizer and FSH-NPK display three regions of weight loss. The first stage of weight loss of FSM (9.6%) detected about 64 ^{o}C whereas, weight loss of FSH-NPK (10.8) occurred below 72 ^{o}C. This first stage could be recognized as water evaporation. However, the first stage of weight loss of NPK fertilizer (30%) between 156 ^{o}C and 227 ^{o}C is associated with degradation of the fertilizer which could be the beginning of the degradation of urea.

The second stage of the weight loss was detected between 64 ^{o}C and 208 ^{o}C for FSM, between 72 ^{o}C and 108 ^{o}C for FSH-NPK, and between 227 ^{o}C and 293 ^{o}C for NPK fertilizer. The weight loss was detected to be 15% for FSH-NPK, 13.7% for FSM, and 32% for commercial NPK. This stage shows the decomposition of organic parts present in the same sample. After these two stages the degradation of FSM and FSH-NPK becomes fast until at 450 ^{o}C. The total weight loss of FSM is about 80.83%, while for FSH-NPK it is about 65%. The final stage of commercial NPK was 41.41%. Overall, the TGA results reveal the total weight loss of FSM is larger than the weight loss of FSH-NPK. This may be due to the crosslinking and the incorporation of NPK into it. From table … the maximum decomposition temperature of NPK was improved in the hydrogel matrix.

Table 4.4. Different % weight lose temperatures

Sample	**$T_{5\%}$(°C)**	**$T_{50\%}$(°C)**	**T_{max}(°C)**
NPK	174.6	----	340
FSM	58.1	307	450
FSH-NPK	50.2	320	450

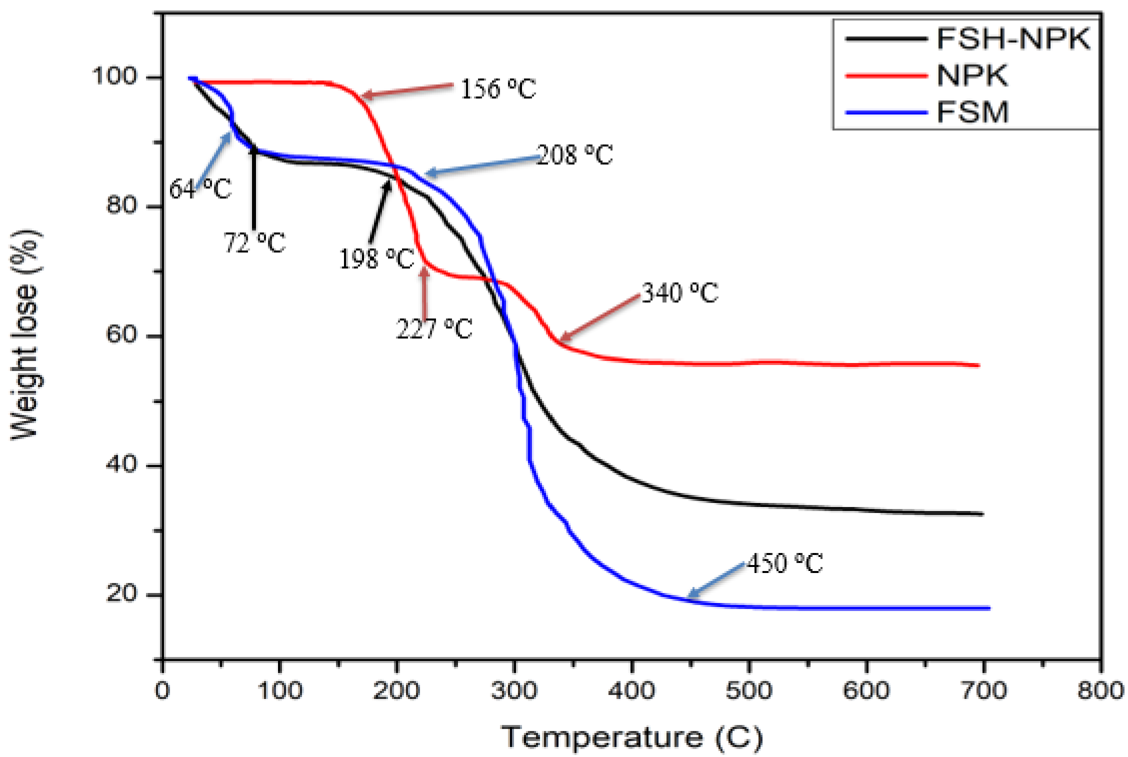


Figure 4.7. TGA analysis of FSM, FSH, and FSH-NPK

4.3.4. X-Ray Diffraction (XRD)

The XRD pattern for flaxseed hydrogel (FSH) and FSH-NPK are displayed in figure 4.8. Pattern of FSH displays broad reflection at $2\theta \approx 22^{\circ}$. This reflects the lack of crystallinity in the formed flaxseed hydrogel. It is probably attributed to irregular brunching polysaccharide structure and the presence of electrostatic repulsion between anionic chains (Hadad & Goli, 2018) (Mirbahoush et al., 2019). The XRD pattern of FSH-NPK is also shown in figure 4.8 it could be observed that there are intense peaks which can be attributed to the loading of NPK fertilizer.

The peaks at 2θ = 22.6˚, 25 ˚, 29 ˚, 32 ˚, 36 ˚, and 37 ˚ can be related to the presence of urea (Olad et al., 2018). Whereas, 2θ = 24˚, 31 ˚, 34 ˚, 46 ˚, 47 ˚ and 2θ = 29 ˚, 41 ˚, 50 ˚ are related to the crystalline of KH_2PO_4 and KCl, respectively (Olad et al., 2018).

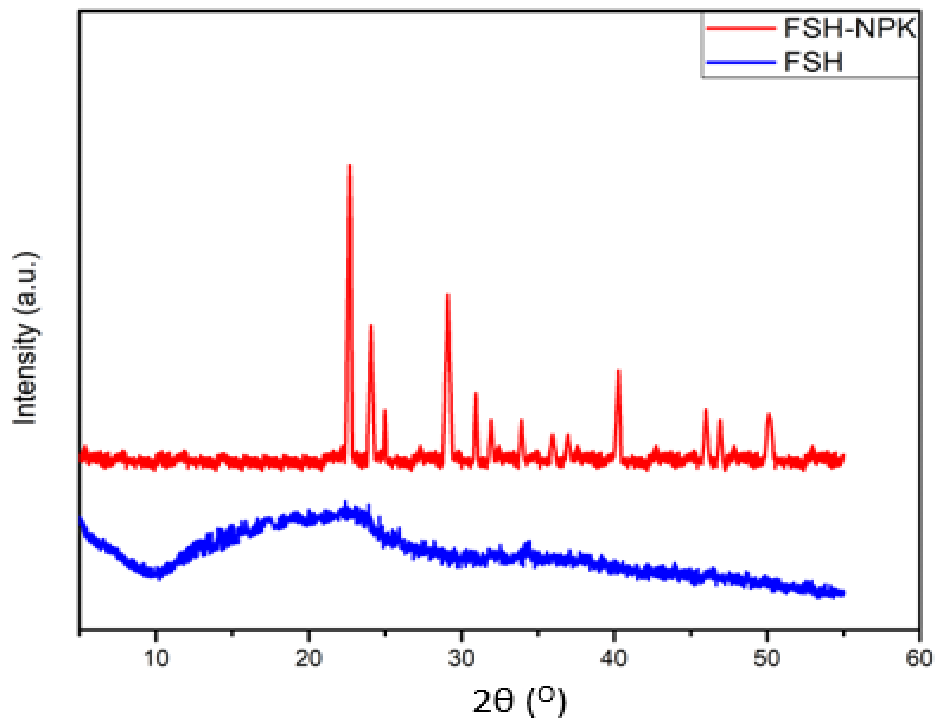


Figure 4.8. XRD analysis of FSH and FSH-NPK

4.4. Swelling analysis

From the swelling analysis it ccan be seen that the FSH can absorb up to 2000% its weight. But, this water absorbance starts to decrease as the NPK loading increase. This can be explained by the occupance of the free space in the three dimensional space with fertilizer. Therefore, there will be less space for the water.

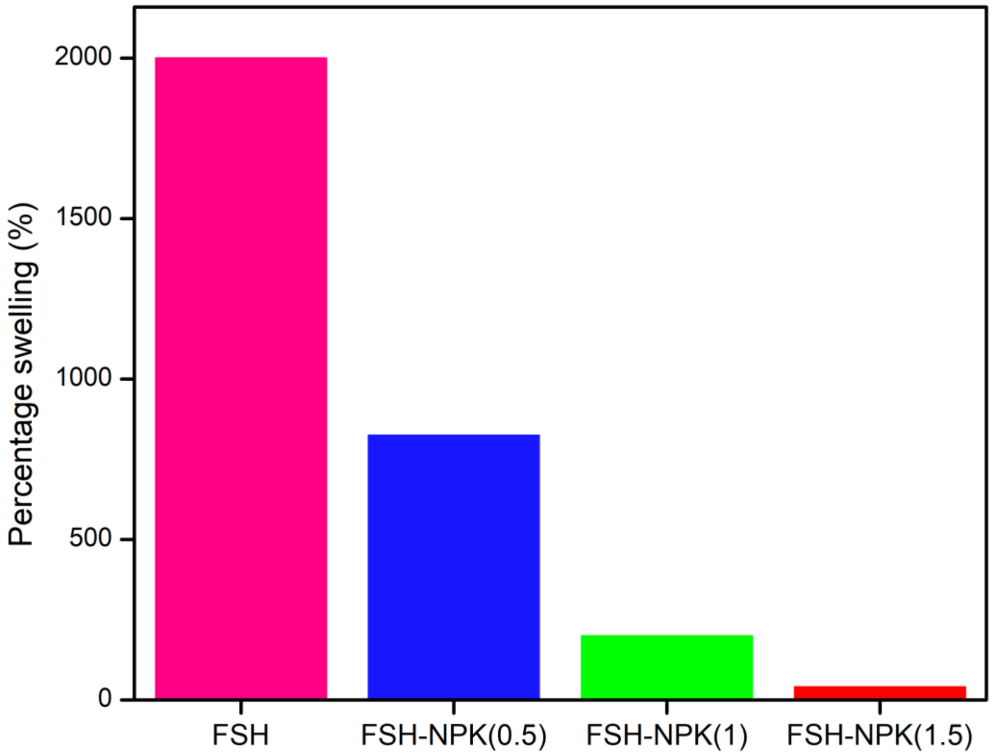


Figure 4.9. Swelling percentage of FSH and different FSH-NPKs.

4.5. Biodegradability

The soil burial method is a common approach to investigate the biodegradation of flaxseed hydrogel. In this method, the hydrogel is buried in the soil for a certain period of time, during which the microorganisms present in the soil break down the hydrogel. The rate of biodegradation can be determined by periodically retrieving the hydrogel from the soil, cleaning it to remove any soil debris, and measuring their weight loss. The soil burial method is often used to evaluate the biodegradability of flaxseed hydrogel and other biodegradable materials under natural environmental conditions. Photographs of flaxseed hydrogel on day 1, day 21 and day 49 of the soil burial test and their subsequent weight loss (%) are depicted in Fig. 10. FSM has a faster degradation rate than the cross-linked hydrogel. lIt only lasted 4 days. On the other hand, when FSM was cross-linked using citric acid, a different outcome was observed. These citric acid cross-linked FSM exhibited slower rates of degradation compared to their counterpart. The crosslinker's concentration also affects the degradation rate. As it can be seen on figure 4.11, as the crosslinker concentration increase, the degradation rate became slow. FSM crosslinked witth 5% citric acid (CA) degraded within 21 days. But, as CA concentration increase to 10%, the degradation lasted 42 days. When CA is 15%, the degradation lasted for 49 days. So, it can be concluded that increasing crosslinker concentration slows the degradation rate.

a b c

Figure 4.10: biodegradation of FSH in soil on the a) 1st day; b) 21st day; c)42nd day

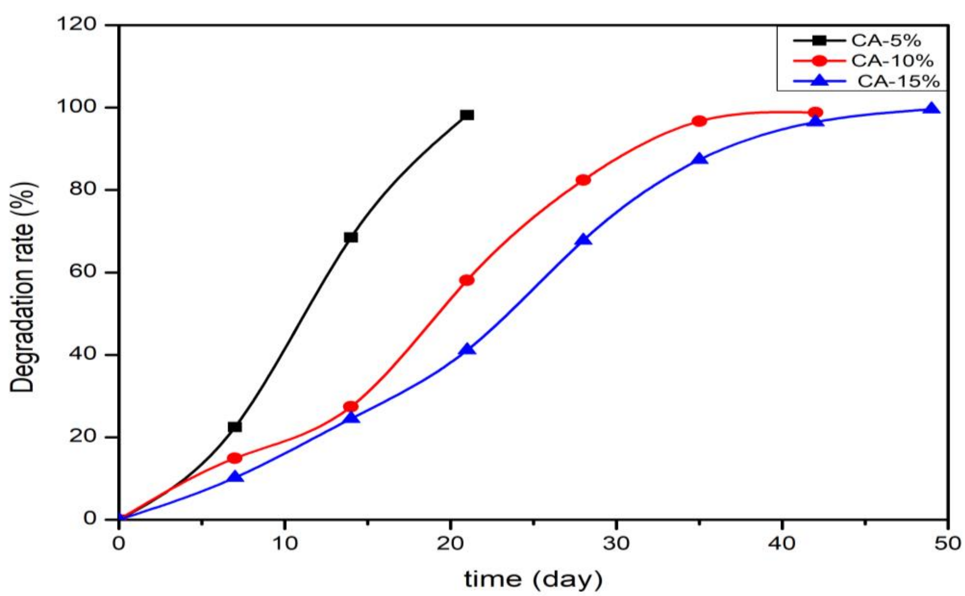


Figure 4.11: biodegradation of FSH in soil

4.6. Release rate

The fertilizer release profile of FSH-NPK formulation was studied in soils with pH of 5, 7, and 8.5. Figure 4.12. Shows the amount of fertilizer released as a function of time. As can be seen, the cumulative release rate of pure NPK is high initially, which is related to the ease of dissolution of fertilizer compound. However, the complete fertilizer release of untreated NPK is reached within 3 days. In contrast, the FSH-NPK formulation fertilizer release on the 3rd, 7th, and 28th days was about 1.34%, 8.04%, and respectively. The obtained results from cumulative release of fertilizer in soil demonstrate that the sum of fertilizer release for FSH-NPK formulation was lower than 15% on the first day and was not above 75% on the 1 month. This finding indicates that the slow release character of the FSH-NPK formulation prepared in this work has a good compliance with the standard of slow release fertilizers of the Committee of European Normalization (CEN) (Trenkel, 1997).

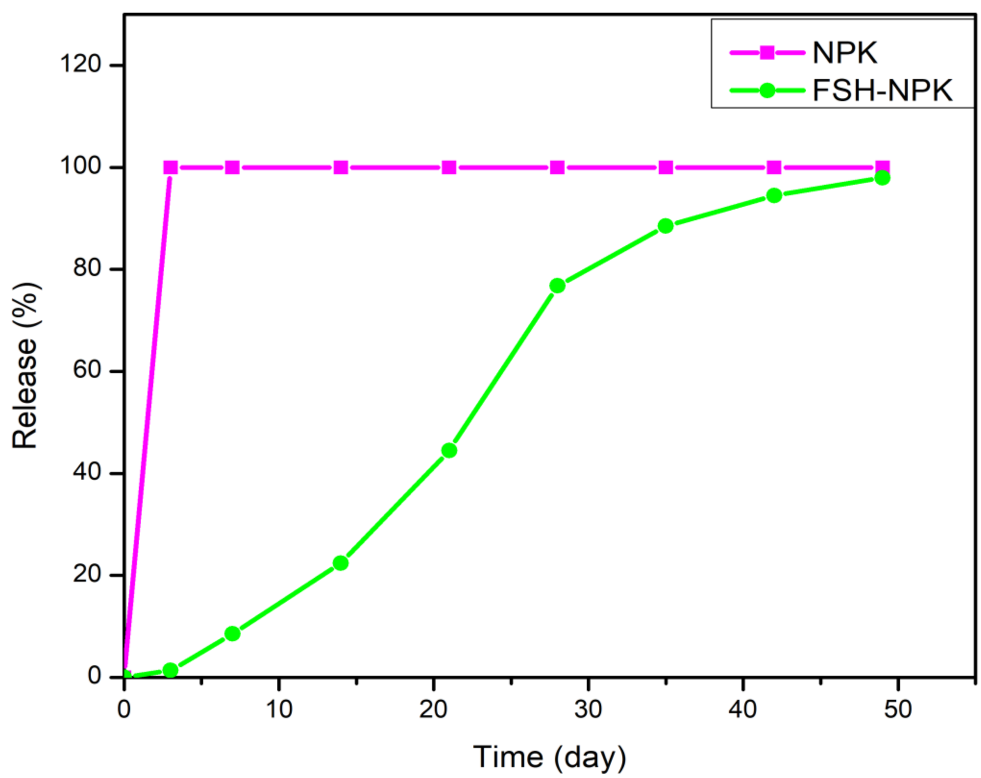


Figure 4.12. NPK release from pure NPK and FSH-NPK

Also, the kinetic of release data of fertilizer from prepared formulations were analyzed by using the more generalized form proposed by Korsmeyer and Peppas (release kinetics, 2018)

$$\frac{M_t}{M_\infty} = K_{KP} t^n \qquad \text{Equation 4.1.}$$

Where ($Mt/M\infty$) is the released fraction of fertilizer at time t, K_{KP} is a constant incorporating characteristic of the macromolecular network system and fertilizer, n is the diffusional exponent which is indicative of the transport mechanism. The value of $n \leq 0.5$ means that the fertilizer release mechanism approaches to a Fickian diffusion controlled release, whereas an n value of $n = 1.0$ indicates that the fertilizer release mechanism approaches to Case II transport (zero order) and the n value between 0.5 and 1.0 shows that fertilizer release mechanism is anomalous (non Fickian) diffusion whereas, when $n > 1$, then the release mechanism becomes degradation. To find the parameters n and K, the equation has to be linearized as equation 4.2.

$$\text{Log}\,(Mt/M\infty) = \text{Log}\,K + n\text{Log}\,t \qquad \text{Equation…4.2.}$$

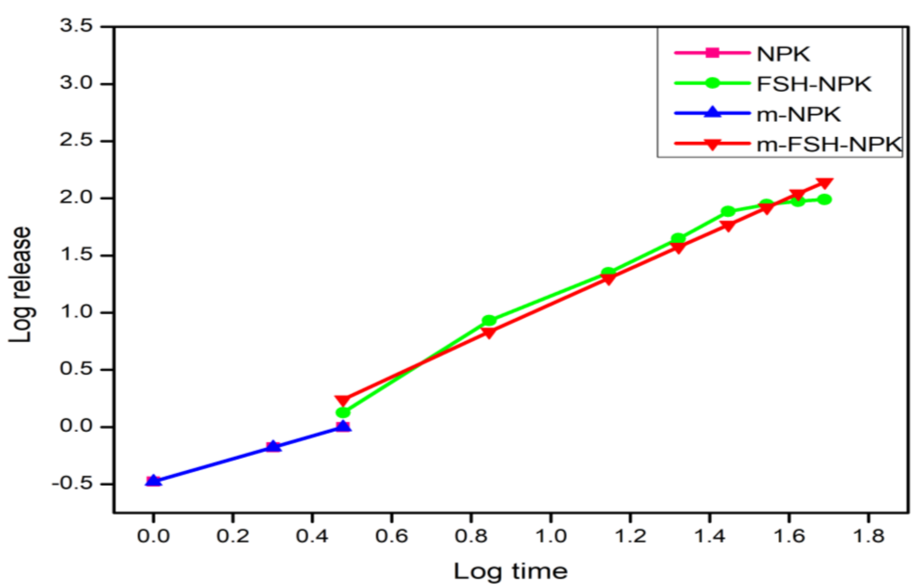


FIGURE 4.13: modelled graph of NPK release

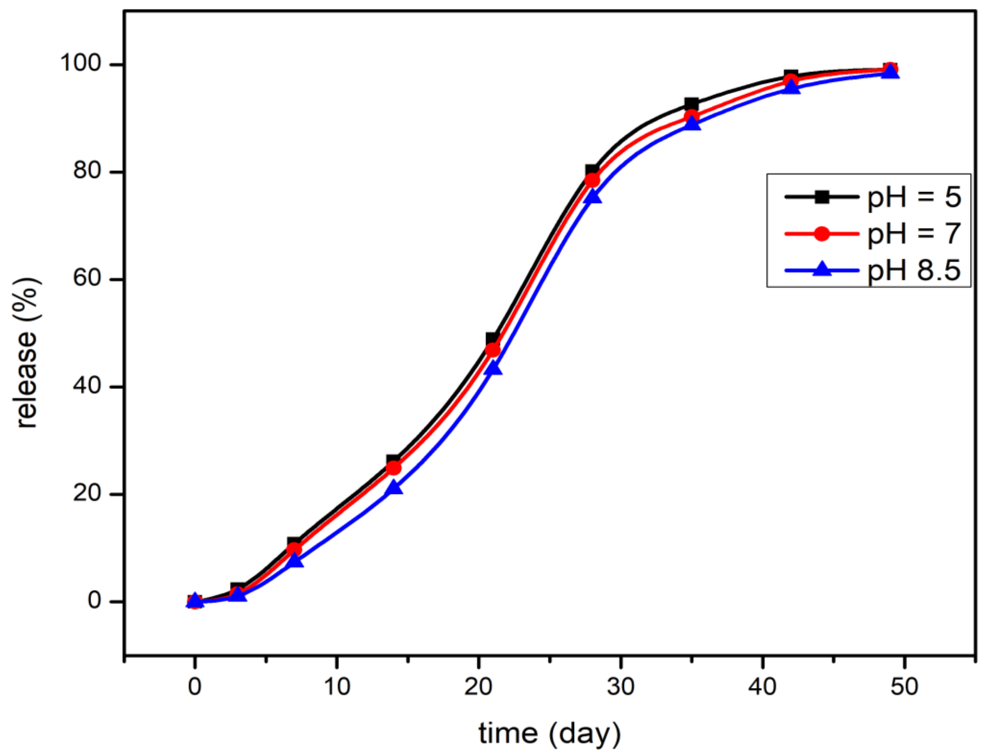
Table 4.5. Kinetic model of NPK release.

Formulation				
Kinetic model	Equation	Parameters	NPK	FSH-NPK
Korsmeyer-Peppas	$\frac{M_t}{M_\infty} = K_{KP} t^n$	R^2	0.9999	0.987
		N	1.0000	1.555
		K × 10	3.3304	3.305

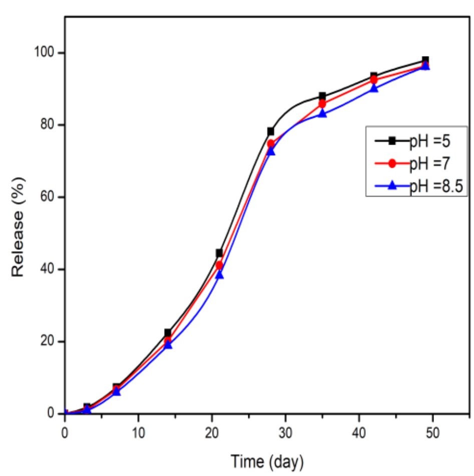
Figure 4.14 shows the release of N, P, K studied in different pH of soils. On acidic soil with pH of 5, nitrogen, phosphorous and potassium were released slightly faster than the neutral soil. On the other hand, the N, P, and K- release was slightly slower in basic medium (pH = 8.5). The kinetic parameters shown in table 4.6 indicates the n value of all nutrients release is greater than 1. This implies that, the release mechanism is degradation and a release by diffusion is insignificant.

Table 4.6: kinetic models of N, P, and, K at different pHs.

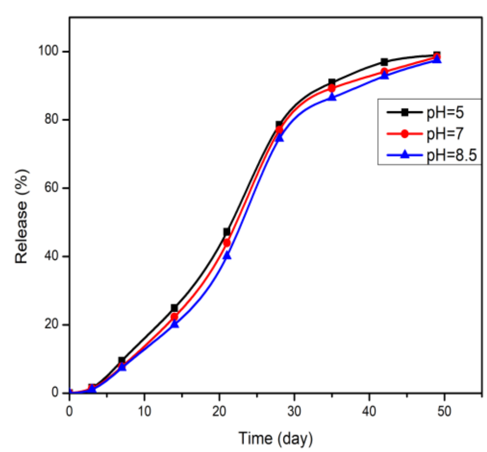
Formulation						
Kinetic Model	**Equation**	**Ph**	**Parameters**	**N**	**P**	**K**
Korsmeyer-Peppas	$\frac{M_t}{M_\infty} = K_{KP} t^n$	**5**	**R^2**	**0.9895**	**0.991**	**0.9867**
			n	**1.369**	**1.496**	**1.4965**
			K × 10	**6.601**	**3.9965**	**4.192**
		7	**R^2**	**0.9857**	**0.9844**	**0.9892**
			n	**1.5074**	**1.668**	**1.5546**
			K × 10	**4.039**	**2.275**	**3.296**
		8.5	**R^2**	**0.9873**	**0.9905**	**0.9882**
			n	**1.6376**	**1.6742**	**1.6309**
			K × 10	**2.468**	**2.024**	**2.448**



a)



b)



c)

Figure 4.14: release rate of N (a), P (b), and K (c) at different soil pH.

4.7. Water retention analysis

Figure 4.15 illustrates the water retention behavior of FSH-NPK formulations in loamy sand soil. Experimental results show that the addition of prepared formulations into loamy sand soil composition increases the water retention of the soil for a longer period of time whereas unmodified soil completely vaporized the absorbed water after 14 days. In addition, it can be seen that the use of FSH-NPK formulation in soil can decrease irrigation frequencies and enhance the ability of plants to fight against drought.

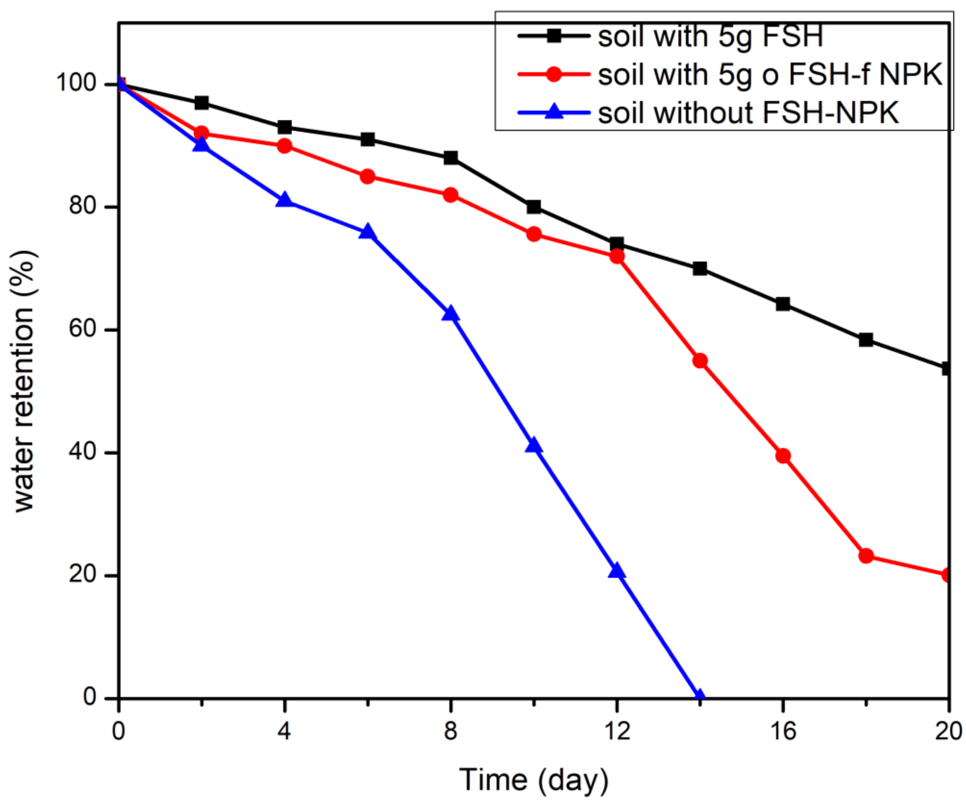


Figure 4.15 water retention of soil without and with FSH and FSH-NPK

From the figure it can be understood that FSH-NPK can improve the water retention capacity of soil, thus, storing water during irrigation or rainfall, and releasing water when facing water stress. For the soil without FSH-NPK, the water retention capacity was 41% on the 10th day and decreased to zero on the 14th day. For the soil with 5g FSH-NPK added, the water retention capacity was 75.6% on the 10th day, and it could still be maintained at 20.1 % on the 20th day. The results showed that the addition of FSH-NPK was beneficial to reduce the speed of water loss and alleviate water stress. It has been found that the water retention performance of soil with SRF was significantly higher than that of soil without SRF. The FSH showed a great potential in retaining water. More than 50% water was retained in the 20th day. This hydrogel can be used in drought stricken areas.

4.8. Pot experiment

To study the effect of FSH-NPK on the growth of barley seed, 3 pot experiments were carried out. The first pot was a control sample (soil without any fertilizer). The second pot was soil with commercial NPK, and the third pot was soil with FSH-NPK. The first parameter studied was the germination rate of barley seed. Each pot was sown with 45 seeds of barley. from the 45 seeds, number of germinated seeds in the 2nd day were 12 in the second pot and 5 in the third pot whereas the first pot didn't have a germinated seed until the 4th day. On the 7th day, a total of 30 seeds in the first pot, 42 seeds in the second pot and 40 seeds in the third pot were germinated. As it can be shown from figure… the germination rate of the 1st pot was only 66.67% after 10 days. On the other hand, the second pot had the highest germination rate (93.33%) within 7 days. the fast and more efficient of germination of the second pot can be explained with the fast release of nutrients from the commercial NPK. The third pot, which contains FSH-NPK showed an 88.89% of germination rate within 7days which is significantly higher than the control. So, it can be concluded that FSH-NPK promotes the germination rate of barley seeds. The highest germination rate was achieved in 10 days for the control pot (the 1st pot), whereas, highest germination was achieved in 7 days on the 2nd and 3rd pots. This indicates that FSH-NPK can promote higher germination rate within a faster time than the soil without any fertilizer (the first pot). It also shows that FSH-NPK have a comparable result in promoting germination rate within the same period of time.

Figure 4.16: germination of barley seed after 7 days.

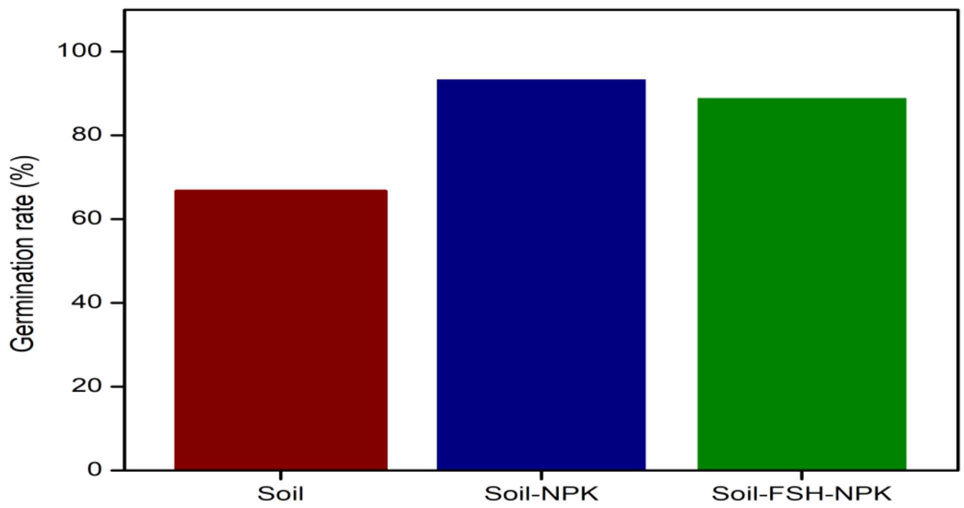


Figure 4.17. germination rate of pot experiment

a b c

Figure 4.18: pot experiment after 21 days a) control, b) NPK, c) FSH-NPK

As it can be seen from figure 4.18, the growth of the first pot after 21 days was slow and the seeds didn't have a uniform growth. On the contrary, the second pot with commercial NPK had a faster and better growth compared to the other two pots. This is due to the ready availability of the major nutrients and trace elements (micronutrients) such as zinc, iron, manganese, copper and molybdenum. The third pot with FSH-NPK had shown a faster and more uniform growth amongst the seeds. But, when compared to the second pot, it has a thinner leaf and shorter height.

After 28 days, the control pot (the first pot) barley seeds became weak and wilted. The unavailability of sufficient nutrients in the soil could contribute to the weakness. The second pot with commercial NPK fertilizer had slower growth. This result showed that after some time, the fertilizer availability diminishes and its growth could become slower. The third pot with FSH-NPK, on the other hand, showed a rapid growth as the release of NPK reached 76%. The barley crops became higher than the 1st and 2nd pot. Whereas, the leaf size and number was more than with the first pot and the second pot.

Figure 4.19 pot experiment after 28 days. a) Control, b) NPK, c) FSH-NPK

After the 28th day the water supply was stopped for 21 days to study how the crops respond to drought stress as reported (Abdelghafar et al., 2024). The result showed that the crops in the 1st pot and 2nd pot were dried and couldn't resist water deficiency. Whereas, crops in the third pot with FSH-NPK were able to resist the water deficiency and continued their growth.

Figure 4.20: pot experiment after 21 days without water

To compare the effect of the fertilizers, the average height of the crops and leaf number were measured. Figure 4.21 shows the average height of the crop with respect to time. Height of the crop in control sample is the smallest throughout 5 weeks. After five weeks it became dried. Its maximum height was 17.05cm in week 5.

The second crop in which commercial NPK was applied showed a fast growth up to week 4. It reached 9.2 cm in the first week and 26.18cm in the fourth week. This fast growth can be attributed to the fast release and nutrient availability. However, after the fourth week, its growth was slower. As the nutrients diminished, the growth became stalled. This can be confirmed in week 5 in which its height increased only in 1cm. It also didn't increase the height in the sixth week and it was beginning to dry. Finally, after seven weeks, the crop was completely dry.

Barley crop in the third pot with FSH-NPK showed a slow growth in the first two weeks. Its height reached 10.3 cm in the second week. This can be the result of slow release of the nutrients. On the fourth week, however, the growth showed a tremendous height increase. Its height reached 27.65cm. Its height was 1.47cm larger than the crop in the commercial NPK applied pot. Its height continued until the seventh week. It reached 33.4cm. The crop was not added from the fourth to seventh week. But, it continued to grow. This can be explained by the ability of the fertilizers water retention capacity.

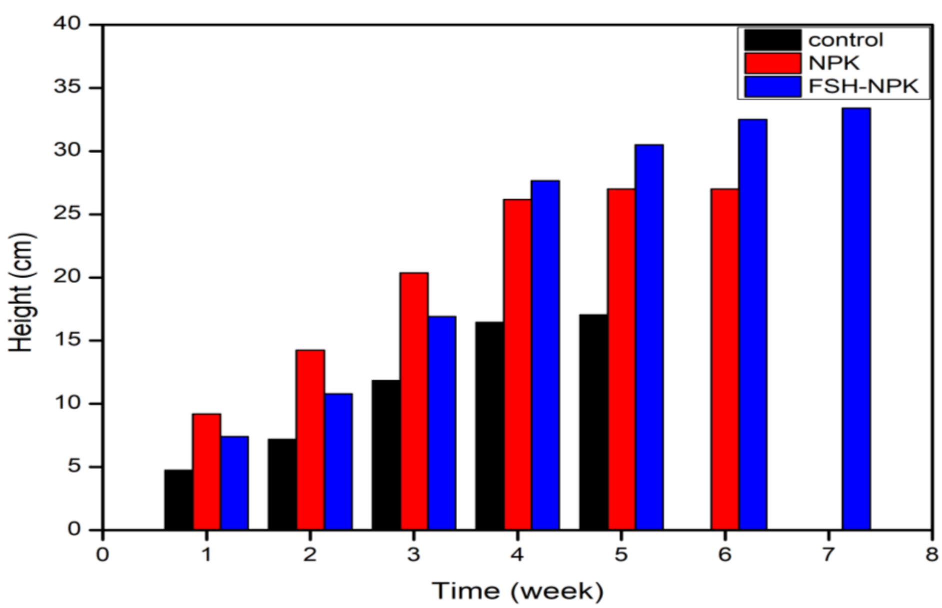


Figure 4.21: Crop height of the sample

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

Flaxseed hydrogel based NPK fertilizer was synthesized to slow the release of nutrients from commercial fertilizers. The encapsulation efficiency was also optimized to 99.5% in 3.687hr, temperature at 69.14℃ and NPK loading of 1.17g. The validation experiment was also carried out in which the encapsulation efficiency have 95.2%.

The water retention and swelling studies were also studied. The results showed that FSH without fertilizer has the highest swelling capacity of 2000%, whereas, FSH-NPK (0.5g) showed a swelling of over 80%. The lowest water absorption was obtained from FSH-NPK (1.5). Which can be concluded as the fertilizer loading increase the water absorption capacity decreases. The water retention studies showed that FSH can be used in drought severed areas as it can contain water over 52% in 20 days.

From the release studies, it can be concluded that the release mechanism is degradation, when the hydrogel degrades, the fertilizer is released. This is proved by Korsmeyer-Peppas model. The nutrients release also showed that with lower pH the release became faster. The degradation and release end within 50 days

The pot experiment also showed that although the growth of barley crop in soil that have FSH-NPK was slower than that of commercial NPK, after 28 days the growth becomes faster and surpasses the growth of the control sample crop and the commercial NPK sample. Therefore, from the results obtained, it can be concluded that the developed can be named as slow release fertilizer and it can have a great importance for the agricultural sector.

5.2. RECOMMENDATION

For future studies, the following recommendation are suggested.

- The pot experiment showed a promising result. For future, it is suggested to study in larger field with different crops.

- The flaxseed mucilage could be used for encapsulation with other polymers to synthesize a composite hydrogel.
- The water retention should be further improved so that it can be applied for drought severed areas.

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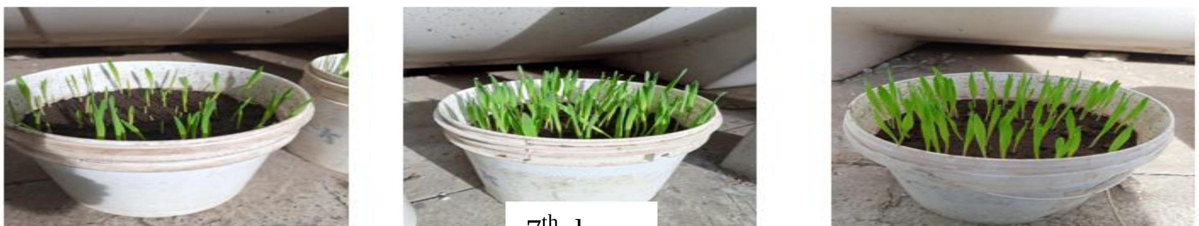
APPENDIX

Growth of barley in different days interval

a. control   b. commercial NPK   c. FSH-NPK

1st day



7th day

21st day

28th day

49th day