

## Synthesis and Characterization of Slow-Release Fertilizer Hydrogel Based on Hydroxy Propyl Methyl Cellulose, Polyvinyl Alcohol, Glycerol and Blended Paper as Second Layer

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### Abstract

In this study, a slow-release urea fertilizer hydrogel was synthesized from hydroxyl propyl methyl cellulose, polyvinyl alcohol and glycerol blends with paper (blended paper) as second layer. The fertilizer hydrogel was characterized by SEM, XRD and FTIR. Its retention in sandy soil, swelling behavior in distilled and tap water as well as slow-release behavior to urea were investigated. The results indicated that the fertilizer had good slow-release properties and ability to retain water in soil. However, the addition of blended paper as a second layer matrix was found to help improve the release properties of the fertilizer. The swelling kinetic of the hydrogel followed the Schott's Second order model. The release kinetics of urea in water was best described by the Zero order model signifying that the release behavior was independent of fertilizer concentration

**Keywords:** Hydrogel, Blended paper, Slow-release fertilizer, Hydroxy Propyl Methyl Cellulose, polyvinyl alcohol.

### 1. Introduction

The world population is growing rapidly and is expected to reach 9.5 billion by the end of 2050 [1]. Meanwhile industrialization, desertification and land degradation caused by heavy flooding have diminished arable land and consequently threatened global food security [2]. Amidst

all these, global food requirements have risen and is likely to double by 2050 [3]. Many steps are being taken to resolve such issues so as to modify and improve our agricultural system and make it more successful and sustainable. To meet the increasing food demand, the agricultural sector is bound to use ever larger quantities of fertilizer that have being demonstrated to have serious undesirable environmental impacts [1]. The use of conventional or mineral fertilizers tends to reach 2.5 million tonnes with subsequent growth of 1.8 percent per year for its demand and supply gap [4].

Despite the use of high quantities of conventional fertilizers, crop utilization is relatively low with subsequent loss to the environment through leaching, denitrification and surface run off [5]. This loss of fertilizer deprives plant of nutrient, increases process cost and causes damage to the environment [6-8]. Recently, to overcome the above-mentioned challenges, intelligent fertilizers such as slow or controlled release fertilizers that supply active nutrients in a slow manner are being researched into and to a limited scale, they are being produced and used [6]. Many studies have shown that slow release or controlled released fertilizer (CRF or SRF) can improve the nutrient use efficiency, reduce damage to crop and environment because it is eco-friendly with minimal pollution [9-13].

Initially Sulphur was used for production of SRF [14] but due to its burst effect, inconsistent result, high cost due to additional requirement of sealants, plasticizers and binders it has been discontinued [5, 15]. However, in place of synthetic polymers, eco-friendly biopolymer such as starch, lignin and cellulose are being used as alternative materials for implementation of SRFs [16-18]. Cellulose is mainly found in high amount in different plant sources where it is cheap, abundantly available and biodegradable [19]. Many efforts are been made to replace synthetic polymers with cellulose derivatives which are used in controlled release for agrochemicals after crosslinking [19]. Hydroxy propyl methyl cellulose (HPMC) is an odourless, tasteless, white to slightly off white fibrous or granular free flowing powder, prepared by modification of alkali cellulose from purified wood pulp treated with 18% sodium hydroxide solution reacted with methyl chloride and propylene oxide to obtain the methyl and hydroxyl ether group and widely used in food, drugs and dietary supplement industries [20]. It is an ideal polymer for film coating which might be used as a basis for hydrophilic matrices for controlled release of drug and fertilizer delivery [21].

Polyvinyl alcohol (PVA) has also been studied for used in fertilizer and drug release since at high content it can control the process release. PVA is a water soluble, semi-crystalline, nontoxic polymer with good physical properties, high ability to absorbed fluid and degrades slowly [22]. It has numerous applications in agricultural industry to deliver fertilizers, pesticide, herbicide [23], extensively used in paper coating, textile sizing, drug release and flexible water-soluble packaging films [22]. Enayatifard *et al.*, [24] studied the effects of HPMC and ethyl cellulose content on release profile and kinetics of Diltiazem HCl from matrices. The results showed that these polymers slowed down the release of Diltiazem HCl from the matrices and could potentially be used for controlled delivery of highly soluble drugs.

HPMC was also used as binder in the preparation of encapsulated urea kaolinite-controlled release fertilizer [9]. Mela and Darajo, prepared controlled release fertilizers using HPMC layered tablets modified with chitosan and xanthan as matrices [25]. Studies by Caccavo *et al.*, produced and characterized hydrogel based granular photo strengthener for prolonged release of fertilizer [26]. PVA and glycerol have been studied for used in controlled fertilizer release [22, 27]. Paper is a mat of cellulose fibers that have been beaten in the presence of water collected on a screen and dried [28]. A paper base typically contains 90-99% cellulose fibers which are the primary structural elements influencing end use properties [29]. Paper network is composed of randomly laid fibrous cellulose and non- fibrous (filler) materials, its complicated set of cavity pore channels having capillary dimensions make it readily permeable to liquids [29]. Hence its structure can be modified during contact of liquids because it disrupts hydrogen bonds, relaxes fibers and produces dimensional changes in pores and capillaries [29].

In our continuous effort [30] to design materials that can effectively deliver urea to plants in a controlled manner, we present here the synthesis and SRF hydrogel based HPMC / PVA / Glycerol with blended paper as the second layer. Furthermore, the effects of use of the blended paper on release, swelling and water retention in soil were investigated.

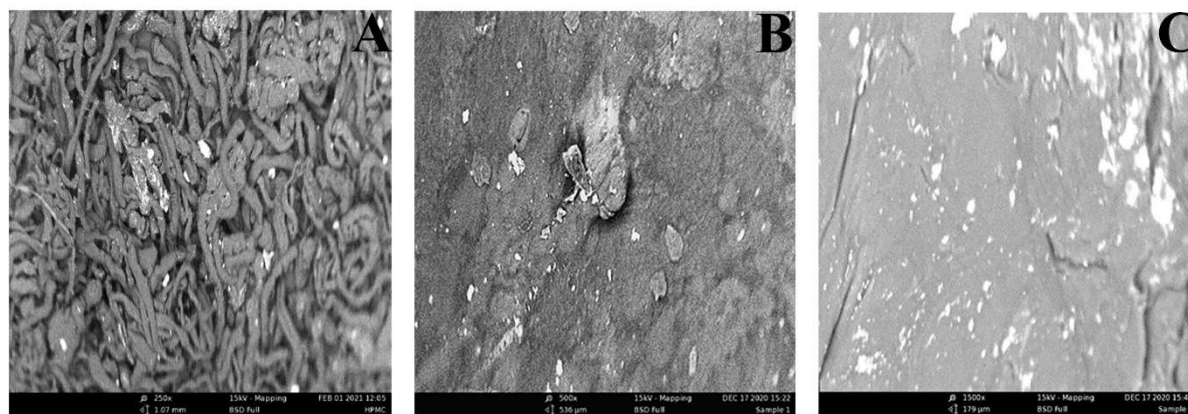
## 2. Results and Discussions

### 2.1 Characterization

#### 2.1.1 Surface Morphology Analysis

SEM technique was used to observe the surface morphologies of the hydrogel (SRF1, SRF2) and the starting materials (HPMC) respectively and results presented in **Figure 1**. From

**Figure 1a**, it can be seen that HPMC powder shows a porous spongy particle like materials which has a rough, less dense surface that are no more recognizable in both hydrogels (SRF1 and SRF2) because of adsorption of urea fertilizer to its surface (microstructure). This porous nature aids to increase the surface area and can enhance the adsorption capacity of HPMC by yielding more sites for more interaction. **Figure 1b** (SRF1) has a uniform and smooth surface without any crack but a pore on the surface. The SRF2 **Figure 1c** shows a rough packed surface having no pores and cracks on the surface which may have enhance its water uptake and retention and consequently the release capacity. The dense and compact structure of the hydrogel is due to the co-polymerization of the polymer and the composite blends resulting from the crosslinking and incorporation of the paper blends into the matrix. This is because polymer matrices can either be chemically cross-linked through covalent or hydrogen bonds [31].

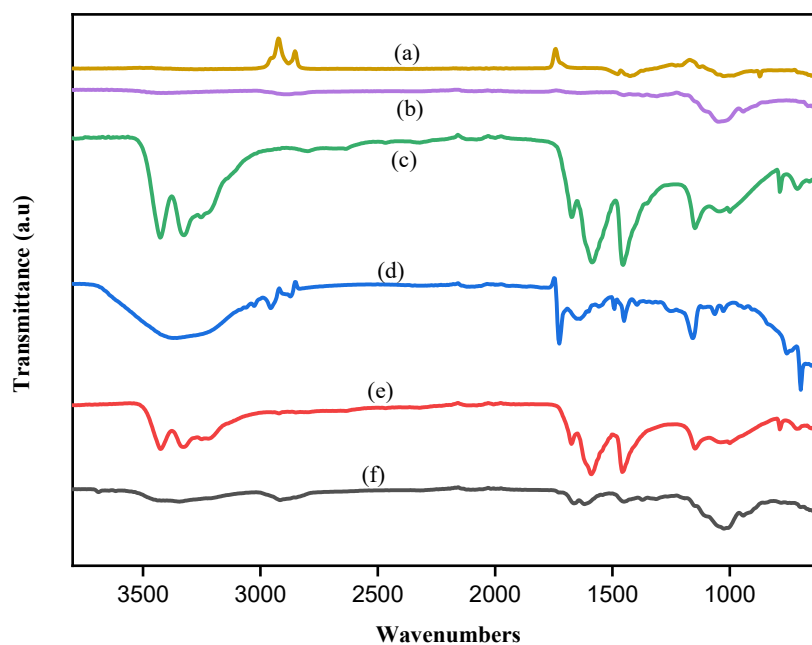


**Figure 1:** SEM Images of HPMC (a) SRF1 and (b) SRF2 (c)

### 2.1.2 FTIR Spectra

The FTIR spectra of blended paper (BP), HPMC, PVA, Urea and SRF's (SRF1 and SRF2) as shown in **Figure 2**. In the spectrum of blended paper (a) peaks at  $3272\text{ cm}^{-1}$  and  $1028\text{ cm}^{-1}$  are associated with stretching vibration of O-H and C-O-C in C-C out of plane stretching vibration [29]. The peaks at  $2759\text{ cm}^{-1}$  and  $2114\text{ cm}^{-1}$  were assigned to  $-\text{CH}-$  in  $\text{CH}_2$  stretching vibration. The absorption band at  $1425\text{ cm}^{-1}$  was ascribed to  $-\text{CH}_2-$  stretching. In the spectrum of HPMC (b) absorption bands at  $3424\text{ cm}^{-1}$  was ascribed to the stretching vibration of O-H. The peak at  $2887\text{ cm}^{-1}$  represents the stretching of  $\text{CH}_2$ , and C=O stretching is observed at  $1648\text{ cm}^{-1}$ . The band at  $1452\text{ cm}^{-1}$  represents  $\text{CH}_2$  and  $1048\text{ cm}^{-1}$  was assigned to C-O-C stretching [32]. In the spectrum of PVA (c), characteristic peaks of PVA occurred at  $3358\text{ cm}^{-1}$  assigned to  $-\text{OH}$  stretching

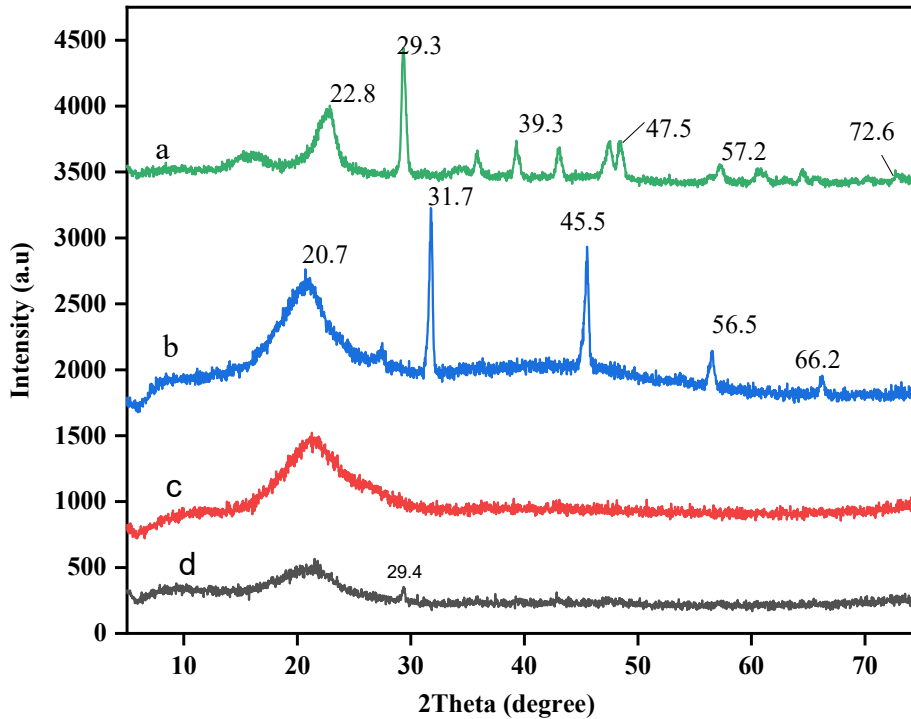
vibration of hydroxyl group in alcohol,  $2956\text{ cm}^{-1}$  –  $2873\text{ cm}^{-1}$  characterized the aliphatic  $-\text{CH}$  symmetric stretching vibration.  $1726\text{ cm}^{-1}$ ,  $1450\text{ cm}^{-1}$  and  $1158\text{ cm}^{-1}$  corresponds to  $\text{C}=\text{O}$  carbonyl,  $-\text{CH}_2$ , and  $\text{C}-\text{O}-\text{C}$  [22]. In the spectrum of Urea (d), two peaks appeared at  $3426\text{ cm}^{-1}$  and  $3326\text{ cm}^{-1}$  related to the stretching vibration of  $-\text{NH}$  and  $-\text{OH}$  group in urea. Furthermore, peaks appeared at  $2799\text{ cm}^{-1}$ ,  $1586\text{ cm}^{-1}$ ,  $1453\text{ cm}^{-1}$ ,  $1148\text{ cm}^{-1}$  and  $1001\text{ cm}^{-1}$  indicating the  $-\text{CH}_2$  stretching vibration,  $-\text{NH}$  angular deformation,  $\text{CH}$  stretching in  $-\text{CH}_2$  aliphatic group and  $-\text{C}-\text{O}$  stretching in  $-\text{C}-\text{O}-\text{C}$  group. In the spectrum of SRF1 (e) and SRF2 (f) new peaks appeared at around  $3425\text{ cm}^{-1}$  and  $3328\text{ cm}^{-1}$  in SRF1 and around  $3689\text{ cm}^{-1}$ ,  $3616\text{ cm}^{-1}$ , and  $3345\text{ cm}^{-1}$  in SRF2 after incorporation of urea into the hydrogel. These peaks may be attributed to the formation of intermolecular hydrogen bond between  $-\text{OH}$  group and the carbonyl group of (PVA and HPMC) [33], and due to the presence of  $-\text{NH}_2$  that is part of  $\text{O}=\text{C}-\text{NH}_2$  functional group in urea [34]. And most of the characteristic peaks shifted to higher frequencies in both hydrogels (SRF1 and SRF2) because the hydrogen bond between water and glycerol was replaced with hydrogen bond between HPMC and glycerol which is weak [22]. The appearance of urea characteristic peaks in FTIR spectra of SRF1 and SRF2 confirms the successful encapsulation of urea fertilizer compound within the matrix hydrogel.



**Figure 2:** FTIR spectra of Blended paper (a), HPMC (b), Urea (c), PVA (d), SRF1 (e), SRF2 (f)

### 2.1.3 XRD Analysis

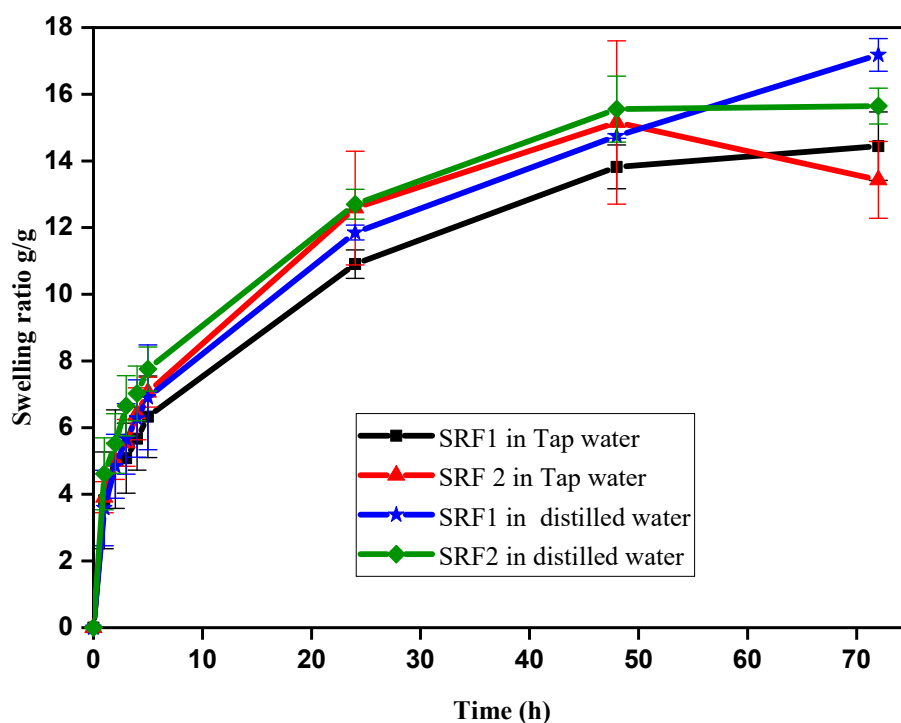
**Figure 3** shows the XRD patterns of blended paper, HPMC and SRF. The characteristic diffraction peaks of blended paper are shown at  $2\theta = 22.8^\circ, 29.3^\circ, 39.3^\circ, 47.5^\circ, 57.2^\circ$  and  $72.8^\circ$ . The XRD pattern of HPMC presents diffraction peaks of cellulose at  $20.7^\circ, 31.7^\circ, 45.5^\circ, 56.5^\circ, 66.2^\circ$  indicating that HPMC is crystalline with crystalline peak. As it can be seen all the samples exhibit typical cellulose diffraction peaks [35]. In the pattern of SRF2, a shift in the basalt diffraction peak from  $29.3$  to  $29.4$  was observed but became weaker. This might be due to high compatibility between the blended paper, HPMC that led to the insertion of paper into HPMC layers which occurred as a result of cationic exchange between hydrogen bond and COO [36]. This slight change indicates that urea was absorbed into the HPMC, blended paper matrix which slowed the release of the nutrient. However, most of the characteristic peaks of blended paper and HPMC were seen to disappear, while in SRF1 no peak was observed with disappearance of characteristic peaks of HPMC. Similarly, a broad peak of amorphous structure of polymer presents shows that compositions of organic materials formed and the blended paper were dispersed in SRF [37].



**Figure 3:** XRD patterns of blended paper (a), HPMC (b), SRF1 (c), SRF2 (d)

## 2.2 Swelling Studies of the hydrogels in Different Solutions

Water absorption is one of the most important characteristics of SRF hydrogels [37]. **Figure 4** shows the water absorption in distilled and tap water. The results shows that the swelling ability in distilled water was higher compared to tap water, this could be as a result of the increase in the osmotic pressure difference between the polymeric network and immersion medium. According to Donnan equilibrium theory, osmotic pressure is the driving force for swelling in hydrogel. The result of this study is consistent with the findings of Enayatifard *et al.*, which shows that the presence of a highly water-soluble compound in HPMC matrix generates an additional osmotic gradient, thereby resulting in a faster rate of polymer swelling and a large increase in gel thickness [24].



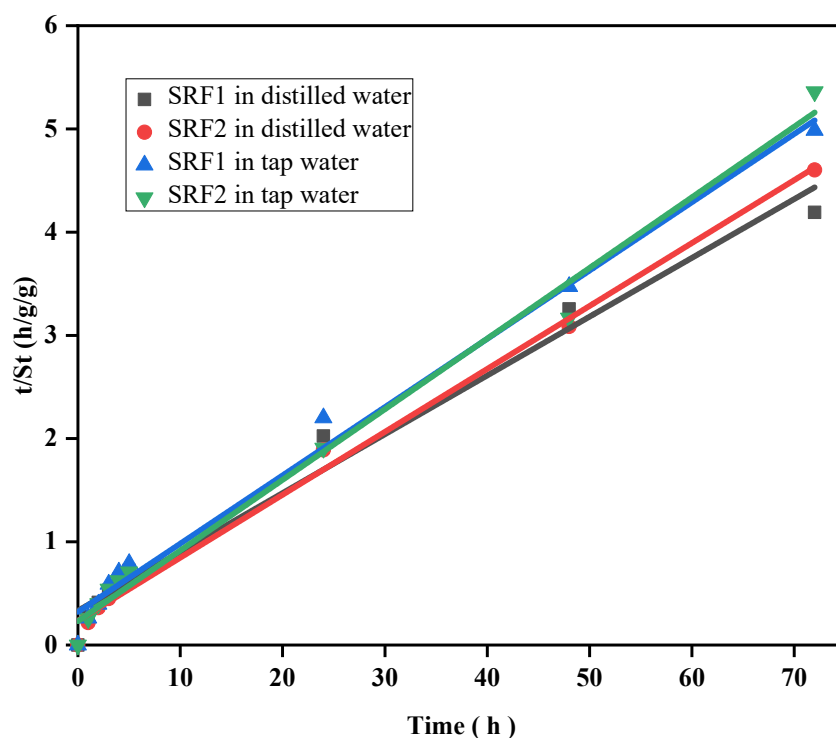
**Figure 4:** Swelling Behaviors of Hydrogels in Solution

Similarly swelling degree might as well be influenced by the ions present in the swelling medium, where by the presence of these ions ( $Mg^{2+}$ ,  $Ca^{2+}$  and  $Na^{+}$ ) increased the ionic crosslinking density of the matrix blend causing a decrease in water absorption as reported by [37]. This observation is common in ionic hydrogels static swelling experiments [38]. The swelling equilibrium of the SRF's hydrogel in both medium was attained at 72 hours except SRF2 in tap water which attained its equilibrium at 48hrs with swelling rate of 17.2 (g/g) and 15.6 (g/g) for SRF1 and SRF2 in

distilled water while 14.4 (g/g) and 15.2 (g/g) for SRF1 and SRF2 in tap water respectively. The swelling rate of SRF2 compared to SRF1 in distilled and tap water was high. This might be as a result of the additional hydroxyl group found in network of cellulose paper, since paper network contains randomly laid cellulose fibrous and non-fibrous (filler) materials which contains complicated set of cavity pore channels with variety of capillaries dimension which make its readily permeable to liquids [29].

### 2.3 Swelling kinetics

The swelling kinetics of the hydrogels in tap and distilled water was determined and the result is shown in **Figure 5**. A straight-line graph was obtained from the plot of  $t/St$  versus  $t$  with a good linear correlation coefficient as given in **Table 1**.  $S_{eq}$  and  $K_{is}$  were calculated from the slope and intercept obtained from fitted straight lines. The result shows that the swelling behavior of hydrogel in distilled and tap water matched the Schott's Second Order swelling kinetic model. The data presented for  $S_{eq}$  and  $K_{is}$  in tap water were lower compared to that in distilled water.



**Figure 5:** Swelling Kinetics of Hydrogel in Solution

**Table 1:** Swelling Kinetic Parameters for the Hydrogels in Distilled and Tap Water

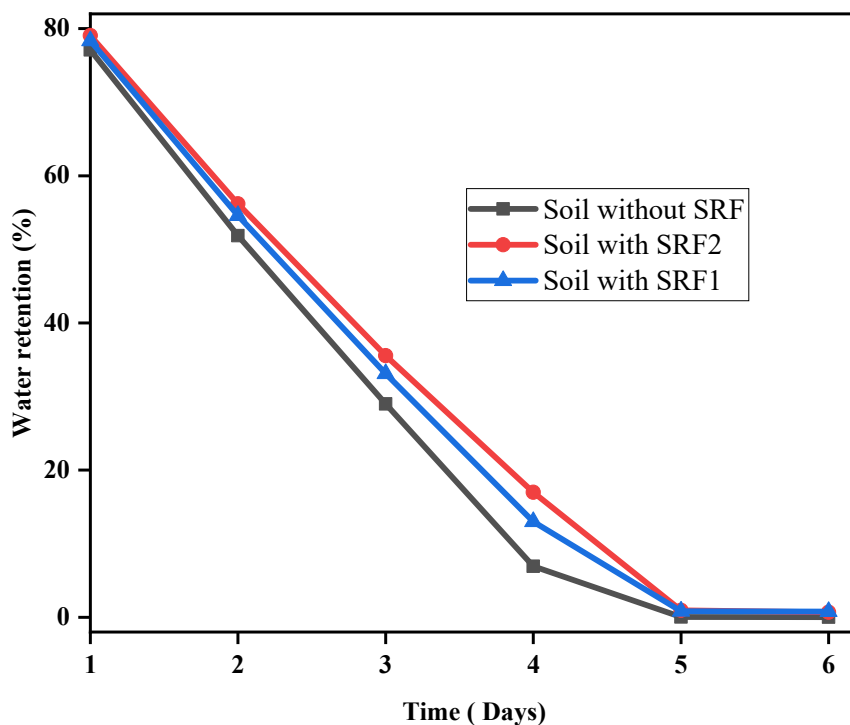
Conditions	Parameters	SRF1	SRF2
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Distilled water	$S_{eq}$ (g/g)	17.56	16.40
	$K_{is}$ (g/g)	3.00	4.23
	$R^2$	0.98052	0.98955
Tap water	$S_{eq}$ (g/g)	15.11	14.61
	$K_{is}$ (g/g)	3.12	4.32
	$R^2$	0.98909	0.99373

#### 2.4 Water Retention Properties of the SRF Hydrogel in Soil

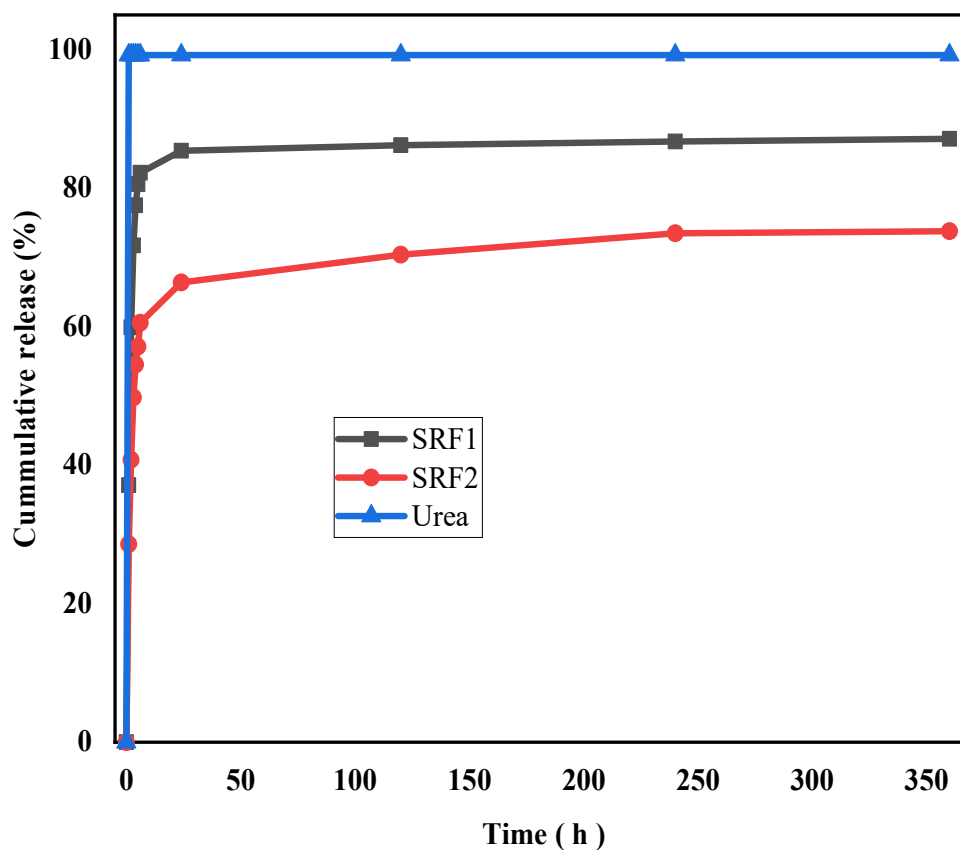
Water retention of hydrogel is an important feature of SRF in soil. **Figure 6** shows the water retention behaviour of sandy soil with and without SRF. By adding the hydrogel in soil, the water retention increased for some time while the water content of soil without the SRF completely vaporized after the 6<sup>th</sup> day. The water retention of soil containing SRF2 was high compared to the soil with SRF1. The water retention ratio of soil without SRF hydrogel had only remained 51.9 and 0.04 on the 2<sup>nd</sup> and the 5<sup>th</sup> day respectively, while that with SRF1 and SRF2 remained 54.6, 0.8 and 56.2 ,1.0 respectively. A similar phenomenon was also found by others [39]. This study finds out that that the addition of blended paper in SRF2 as second layer helps in increasing the water retention in soil and decreases water transpiration. That is, it withholds sufficient water which would aid efficient utilization of it for crop cultivation there by minimize irrigation water for farming.



**Figure 6:** Water Retention Behaviour of Sandy Soil with and without Hydrogel

### 2.5 Release Profile of SRF Hydrogel and kinetics of release.

Nutrient release profile was important to determine if the encapsulation was suitable for slow fertilizer release [40]. The cumulative release rate of different types of hydrogel fertilizer in water is shown in **Figure 7**. The release rate of pure urea reached 99% within one hour. The nutrient release of SRF2 was slower compared to SRF1. The release fraction of SRF2 and SRF1 within 1, 6 and 24 hours were about 28.6%, 59.6%, 64.4% and 37%, 82.2% and 85.4% respectively. This is because the use of blended paper and HPMC as second layer matrix made the urea release slower, which might be due to physical barrier of the hydrogel matrix and the intermolecular hydrogen bond between the blended paper and urea [29]. This agrees with Liu *et al.*, who reported that increase in the membrane resistance of the matrix that withstands the osmotic pressure results in slower release of the nutrient by diffusion forced by a concentration or pressure gradient or the combination of the two [41]. The release data of the hydrogels in water were analyzed using four different kinetic models. **Table 2** shows the kinetic parameters of each of the model equations used. The results show that zero order kinetic equation was the most suitable model for describing the release mechanism of the fertilizer in water ( $R^2 > 0.851$ ), which indicates that the release rate of urea in water is independent of its concentration [42].



**Figure 7:** Release Behavior of Urea, SRF1 without Paper and SRF2 with Blended Paper in Water

**Table 2:** Kinetic parameters of each of the model used

Kinetic models	Parameter	SRF1	SRF2
Korsmeyer –Peppas	$R^2$	0.85101	0.71925
	n	0.6842	0.5027
	$K \times 10^2$	0.50	0.45
Higuchi model	$R^2$	0.85108	0.71925
	$K \times 10^2$	0.19	0.14
Zero order model	$R^2$	0.85108	0.71925
	$K \times 10^2$	0.19	0.14
First order model	$R^2$	0.5958	0.6686
	$K \times 10^{-2}$	0.95	0.81

### 3. Conclusions

In this work, slow release and water retention fertilizer hydrogels from hydroxyl propyl methyl cellulose (HPMC)/ polyvinyl alcohol (PVA)/ Glycerol was prepared with blended paper as second layer matrix which encapsulated urea fertilizer. The hydrogels were analyzed by SEM and XRD. The water absorption in different media and water retention in soil were calculated. The SEM and XRD characterizations confirmed that urea had been successfully absorbed or encapsulated within layer of the matrix, and paper had been introduced into the fertilizer. The swelling behavior of SRF was studied in distilled and tap water. The SRF2 hydrogel had water absorbency of 15.6 (g/g) and 15.2 (g/g) in distilled and tap water respectively. The water retention was found to increase when SRF hydrogels were added to the soil. Similarly, the slow-release behavior of urea was studied in distilled water. As expected, the swelling ability in distilled water was higher compared to tap water. The swelling kinetics of the hydrogel followed Schott's second order equation. The cumulative release fraction of urea was slower for SRF2 compared to SRF1. This might be due to the addition of blended paper as second layer which slows the release rate of urea in the SRF hydrogels. The release kinetic of urea follows zero order kinetic model with ( $R^2 = 0.851$ ). These results suggest that the hydrogel SRF from HPMC/PVA/Gly with paper as second layer will go a long way to improve agricultural and horticultural productivity through efficient fertilizer utilization and improved water conservation thereby reducing the amount of urea fertilizer and water for irrigation purposes.

### 4. Materials and Methods

#### 4.1 Materials

Hydroxy propyl methyl cellulose (viscosity 25-100mpa.s) was purchased from Shanghai Chemical Factory, Shanghai, China. Polyvinyl alcohol and Glycerol were purchased from Guangdang Guanghua Chemical Factory, co ltd, Shanfai, China and Kermel. A4 Paper was obtained from a business center, Modibbo Adama University commercial center Yola, Nigeria. Thiosemicarbazide, deacetyl monoxime, Phosphoric acid and Sulfuric acid were obtained from commercial outlet. All chemicals' reagents were of analytical grade and were used without further purification. Distilled water was obtained from Chemical Engineering laboratory, Modibbo Adama University, Yola, Nigeria and was used throughout the experiment.

#### 4.2 Preparation of SRF Hydrogel Based on HPMC, PVA, Glycerol with Paper as Second Layer

Calculated amount of HPMC, PVA and Glycerol were mixed at various ratio and 50 mL distilled water was slowly added to the mixture at room temperature under magnetic stirring for 20 minute to form dispersion. When completely mixed, the temperature of the mixture was slowly raised to 90°C maintaining stirring for another 5 minutes to completely gelatinize the HPMC. Two grams (2g) of urea fertilizer was thoroughly blended with the mixture with glass rod, there after it was dried at 25°C forming a single layer matrix. The above procedure was repeated and blended with 0.5g of paper as the second layer and as well without paper as the second layer. The matrix was later dried at room temperature and then oven dried at 50°C for 4h. **Table 4** contains the matrix formulation as reported by Sofyane *et al.*, [22] but with a small modification.

**Table 3:** Composition of the Hydrogels

Sample	HPMC (g)	PVA (g)	Gly (g)	Paper (g)
SRF1	5.0	0.4	0.5	-
SRF2	5.0	0.4	0.5	0.5

#### 4.3 Characterization

The surface morphology of the prepared hydrogels was observed by scanning electron microscope PRO:X: Phenom World (Model:800-07334) with backscattered electrons detector (BSD), electrons beam voltage of 15kV. The FTIR spectra of the HPMC, PVA, blended paper and hydrogels matrix were measured by Shimadzu Fourier transform infrared spectroscopy (FTIR-8400S) at wavelength of 400 to 4000  $\text{cm}^{-1}$  with KBr discs. X-ray diffraction patterns of HPMC, paper and SRF hydrogel were recorded by X-ray diffractometer, thermoscientific (Model: ARL X'TRA) in the  $2\theta$  range of 10° to 70°. Urea content in solution was determined by ultraviolet spectrophotometry (Jenway 6705) based on standard curve of urea obtained using reaction of urea with diacetylmonoxim colorimetric method [9].

#### 4.4 Swelling Behavior of Hydrogels

About 0.5 g of dried samples were weighed and immersed into distilled and tap water enclosed in 200 mesh bags respectively. After regular time intervals the swollen samples were removed from the water and dried off of any excess water with a filter paper and weighed. The water uptake was calculated according to the equation (1)

$$W.A = \frac{M - M_j}{M_j} \quad (1)$$

Where  $M$  and  $M_j$  are weights of swollen and dried samples respectively.

##### 4.4.1 Swelling kinetics

The Swelling kinetics of the matrix was determined using Schott's second order swelling kinetic model given as

$$\frac{t}{S_t} = \frac{1}{K_{is}} + \frac{1}{S_{eq}}t \quad (2)$$

Where  $S_t$  (g/g) is the water absorption capacity at any time  $t$  (h) while  $S_{eq}$  (g/g) stands for the theoretical equilibrium water absorption and  $K_{is}$  (g/g) represents a constant for the initial swelling rate. From the plot of  $t/S_t$  versus  $t$ , a straight line was obtained which shows that the swelling obeys Schott's second order model and the values of  $S_{eq}$  and  $K_{is}$  were obtained from slope and intercept.

#### 4.5 Water Retention of Hydrogels in Soil

Dried samples (0.5 g) were weighed and added into 100 g of dried sandy soil in a 250 mL beaker. At the same time, 100g of dried sandy soil without the hydrogel was put in another beaker as control. Then each beaker was added 50 mL distilled water and weighed. The beakers were weighed every day at room temperature until it got to a constant mass. The water retention  $W_r$  (%) of soil was calculated by equation 3

$$W_r = \frac{W_i - W}{W_o - W} \times 100 \quad (3)$$

Where  $W_r$  is the water retention rate and  $W$  is the total mass of sandy soil and beaker.  $W_o$  is the total mass of sand, beaker and sample after adding distilled water.  $W_i$  is the total mass of sand, beaker, and sample at regular intervals.

#### 4.6 Slow-Release Behavior of Hydrogels

The release behavior of the matrix was first studied in distilled water, where 1 g of dried sample was immersed in a 250 mL beaker placed in a tight container containing 200 mL distilled water. At each preset time interval, the samples were transferred into another beaker containing 200 mL fresh water, this continued until all the urea was released. Then 1 mL of the solution was withdrawn from the beaker and the urea content in the solution was determined by UV-Vis Spectrophotometry using the diacetylmonoxime calorimetry method based on the standard curve obtained.

#### 4.7 Release Kinetic of Hydrogel

The release behavior was analyzed by four different empirical equations that is the power equation by Korsmeyer-Peppas, Higuchi, zero order and first order mathematical models. The power equation is given as equation (4).

$$\frac{M_t}{M_\infty} = K_i t^n \quad (4)$$

Where  $K_i$ ,  $t$ , and  $n$  are diffusion content, time and diffusion exponent indicative of the release mechanism respectively.  $M_t/M_\infty$  is the fraction of fertilizer released at time  $t$ . Nutrient release mechanism is classified according to different values of  $n$ , if  $n < 0.45$ , then it is Fickian diffusion mechanism; if  $0.45 < n < 0.89$  then is non Fickian diffusion release; if  $n=1$  then is zero order release, if  $n > 0.89$  then is case II transport [42].

The Higuchi kinetic model can be written as equation (5)

$$Q_t = K_H t^{1/2} \quad (5)$$

The Zero order kinetic model is given as follows

$$Q_t = K_o t \quad (6)$$

The First order model is given as below

$$Q_t = Q_o e^{-kt} \quad (7)$$

Where  $Q_t$  is the amount of nutrient release at time t,  $Q_0$ , is the amount of nutrient initially in the matrix, t is the time,  $K_H$  is the Higuchi dissolution constant,  $K_0$  and  $K$  is the zero order and first order release constant respectively.

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**Conflicts of Interest:** The authors declare no conflict of interest

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