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Research article

Synthesis and characterization of cellulose phosphate-based superabsorbent hydrogels from rice husk under microwave heating

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ABSTRACT

The current study deals with the synthesis and characterization of superabsorbent hydrogels from rice husk cellulose. Rice husks are slow decomposing waste from the milling of rice with an estimated composition of cellulose (50 %), lignin (25–30 %), silica (15–20 %), and moisture (10–15 %). The aim of using it as a source of cellulose was to provide an alternative use of the otherwise incinerated waste product that is abundantly available in rice producing countries like Kenya. Cellulose-based hydrogels continue to attract interest because of their biocompatibility and biodegradability for which they have found use in several fields including drug release, packaging films, agriculture, among others. The cellulose was extracted from rice husk and crosslinked with phosphoric acid under microwave oven heating. The products were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, x-ray diffraction and x-ray fluorescence. Four parameters namely, heating time, microwave oven power out-put, percent swelling and the amount of cross-linker required for complete reaction were optimized for the synthesis of superabsorbent hydrogels. The optimum percentage swelling was found to be 877 %, heating time of 3 minutes, microwave oven power output of 420 watts (level 6 on the microwave oven dial), 10 mL of cross-linker when 2 g cellulose was used. The efficacy of the hydrogel in maize growing was determined by planting maize in pots in a greenhouse under varied hydrogel dose treatments and measuring growth and yield parameters over a period of twelve weeks. The values of plant growth and yield parameters were found to increase with hydrogel dose with the best results being observed among maize plants grown under the hydrogel dose of 5 g per pot. It was observed that the maize plants in pots treated with hydrogel continued to thrive while those in pots without any hydrogel dried off as expected when rains fail. These results are significant in that they demonstrate that rice husk cellulose-based hydrogels are efficacious in maize growing in a greenhouse.

1. Introduction

Rice husks (also known as rice hulls) are the hard protective coverings of rice grains which are separated from the grains during the milling process to release the brown rice grain. For a long time rice husks, though abundantly available in rice producing regions of the world as agricultural waste material, have had no large scale use. In terms of composition the rice husks are made up of cellulose (50 %), lignin (25–30 %), silica (15–20 %), and moisture (10–15 %) [4]. They are, therefore, not the most cellulose rich source of the natural polymer but because they are abundantly available with little or no large scale use, they are being exploited as a source of cellulose instead of incineration which would lead to air pollution and associated health problems [16, 23]. This will provide an alternative means of rice husks disposal in addition to proving soil conditioning for agricultural production.

Superabsorbent hydrogels are polymers capable of absorbing and retaining extremely large amounts of water. Their hydrophilicity is due to the presence of hydrophilic groups (e.g. OH, COOH, CONH, $CONH_2$, and SO_3H) on the polymer network. Sometimes terms hydrogel and gel are often used interchangeably by biomaterial scientists, to describe crosslinked polymer networks [9]. The crosslinking makes the polymer resistant to dissolution and the degree of the crosslinking determines the physical integrity and the mechanical strength of the polymer [34]. Superabsorbent hydrogels are widely used in various fields such as

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hygiene napkins, disposable diapers, soil for horticulture and agriculture, water purification, food, construction and building, biomedical application and controlled release [43]. Some of these applications demand for biocompatible, and non-toxic hydrogels. Most of the superabsorbent hydrogels known are prepared from synthetic materials or petroleum-based products and crosslinked with polyvinyl alcohol [24], polyamido-amine [11], polyacrylamide [12], poly-N-isopropyl acrylamide [28] and polyethylene glycol [27]. These are known to be toxic and environmentally unfriendly. Cellulose-based hydrogels have attracted much attention due to their non-toxicity, biocompatibility and degradability. Research focus has, thus, shifted to the development of noon-toxic and environmentally safe hydrogels useful for tissue engineering [18], sensors [38], drug delivery [46], among others, for which non-toxicity is essential.

Cellulose is the most abundant natural polymer synthesized by certain organisms ranging from bacteria to plants and animals as an extracellular polymer of glucose molecules for various biological functions [26]. It is water-insoluble, inexhaustible, biocompatible, biodegradable and environmentally friendly [7]. The cellulose unit $(C_6H_{10}O_5)_n$ has three hydroxyl groups (C2, C3 and C6) which are highly polar and reactive [21]. Cellulose is capable of absorbing water, due to the presence of the hydroxyl groups, (as shown in Fig. 1) and can be further modified [35,37].

It is widely spread in plants such as grass [41], straw [48], wood [40] and cotton [22]. Cellulose has been isolated from several agricultural wastes such as, orange peels [6] palms oil [31], banana [2], rice husk [1] cotton waste [13], durian [33], sago waste [32] and bacteria (*Acetobacter*, *Agrobacterium*, *Achromobacter*, *Alcaligenes*, *Aerobacter*, *Azotobacter*, *Pseudomonas* and *Sarcina*). Fig. 1 shows the structure of cellulose.

The reaction of cellulose with phosphoric acid can be obtained by adding 85 % phosphoric acid to cellulose and the temperature is raised to 100 °C for 30 minutes. In this reaction, phosphoric acid will attack the OH group of cellulose chain thereby forming a phosphorous acid group by ester linkage as shown in Scheme 1. The reaction of cellulose and phosphoric acid under molten urea can be obtained by raising the temperature to 140 °C for 30 minutes. The reaction can also be achieved by using dimethylformamide (DMF) as a solvent, cellulose is added to urea for 1 hour, followed by phosphoric acid, stirred for 4 hours at 130 °C. Scheme 1 shows the crosslinking of cellulose with phosphoric acid.

Microwave heating is an alternative source of energy, which is considered as a more efficient method of heating for chemical reactions. According to [25], microwave irradiation fastens conversion and chemical reaction rates.

Several studies have been done on crosslinking of cellulose (hardwood Kraft) but there is limited information on using rice husk cellulose crosslinked with phosphoric acid. Therefore, the aim of this study was to synthesize superabsorbent hydrogels from rice husk by crosslinking it with phosphoric acid, and to optimize the reaction conditions for synthesis under microwave heating. It was also important to evaluate the efficacy of the synthesized hydrogels in growing maize in a greenhouse.

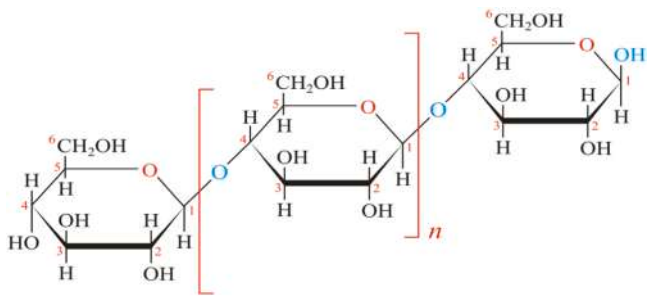


Fig. 1. Structure of cellulose.

1.1. Methods

1.1.1. Extraction of cellulose

About 5.00 g of rice husks were transferred into a 250 mL Erlenmeyer flask followed by 100 mL of 80 % glacial acetic acid and 10 mL of 70 % nitric acid. The flask was covered with aluminium foil and heated in an electric oven at 120 °C for 20 minutes. The mixture was allowed to cool after which 60 mL of distilled water was added and mixed well. The mixture was filtered and the residue washed with 100 mL distilled water and 100 mL 95 % ethanol. The residue was dried in an oven at 60 °C for 19 hrs ([10]; Artanti and Kurniyati, 2016). Fig. 2 shows the process of extraction of cellulose from rice husks.

The yield of cellulose extract was calculated using the formula,

$$\text{The yield of cellulose}(\%) = \frac{\textit{Dry weight extract of RH}}{\textit{Weight of RH}} \times 100\% \quad (1)$$

Plate 1 shows the image of the extracted cellulose.

1.2. Crosslinking of cellulose with phosphoric acid

About 2.00 g of extracted cellulose was suspended in 30 mL of distilled water in a 200 mL beaker and stirred at room temperature for 24hrs. The resulting mixture was treated with 10 mL of 85 % phosphoric acid and heated in a microwave oven at a power output of 420 watts for 3 minutes. The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 °C to a constant weight. The product was characterized by determining its percentage swelling in distilled water, FTIR spectroscopy, and powder XRD.

1.3. Swelling ratio

The equilibrium swelling was measured by weighing the sample before and after exposure to distilled water. The swelling ratio was obtained using the following equation:

$$\%\textit{Swelling}(\%S) = \left(\frac{m_t - m_o}{m_o}\right) x100 \quad (2)$$

where, m_o is the initial weight of the hydrogel (before swelling) and m_t is the final weight of the hydrogel (after swelling).

1.4. Characterization of superabsorbent hydrogel

1.4.1. Fourier transform infrared (FTIR) spectroscopy

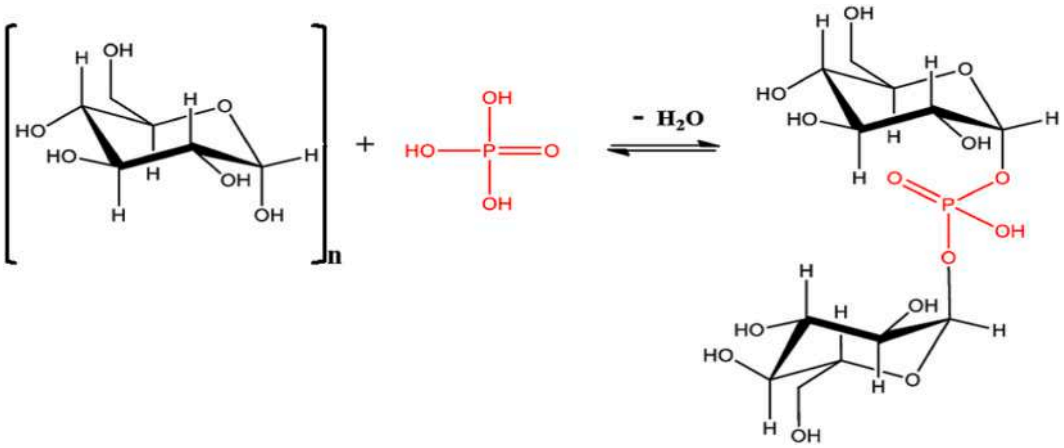
The infrared spectra of the rice husk cellulose and synthesized hydrogels were recorded on a Shimadzu IRTracer-100 spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region.

1.4.2. X-ray diffraction (XRD)

The diffraction patterns of the extracted cellulose and cellulose crosslinked with phosphoric acid were recorded on a D2 PHASER Bruker AXS X-ray diffractometer in scattering angle (2θ) range of 10–60° at a scan rate of 5°/min. The powdered samples were dried in a hot air oven at 105 °C for 3 hours before recording the diffraction patterns.

1.4.3. Scanning electron microscopy (SEM)

The surface morphology of the cellulose was studied on a Jeol JSM-6490A scanning electron microscope at an accelerating voltage of 5.0 kV. The images were captured at different magnifications (5.00 kx, 1.00 kx, 200 x etc.).



Scheme 1. Crosslinking of cellulose with phosphoric acid.

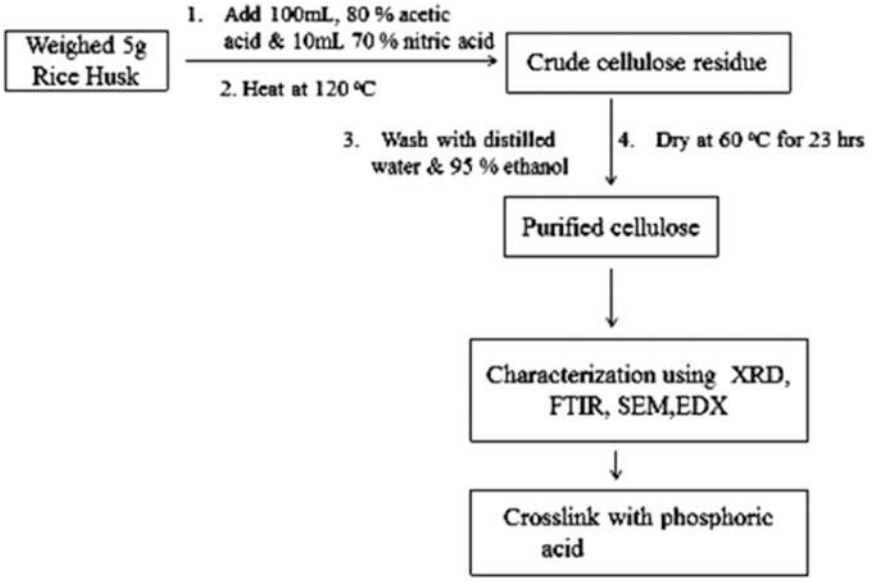


Fig. 2. The cellulose extraction process.



Plate 1. Extracted cellulose from rice husk.

1.5. Optimization of reaction conditions for synthesis of superabsorbent hydrogels (SAHs)

The reaction time, microwave oven power out-put, and amount of cross-linker required were optimized by preparing the hydrogels under different conditions and determining the percentage swelling of SAH prepared under varied condition as described below. The parameters that gave the hydrogel with the highest percentage swelling were selected as the optimum synthesis conditions.

1.5.1. Optimization of reaction time for the cross-linking of cellulose with phosphoric acid

To determine the optimum reaction time for completion of the reaction, the phosphoric acid SAH was prepared under varied reaction times i.e. 1–5 minutes while other conditions were kept constant and percentage swelling of each product was determined. In a typical synthesis, 2.00 g of cellulose was suspended in 30 mL of distilled water in a 200 mL beaker and treated with 10 mL phosphoric acid. The mixture was heated in a microwave oven at a power output of 420 watts for a given period of time e.g. 3 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was wash several times with distill water and dried to a constant weight in an oven at 40 °C. The synthesis experiments were carried out in triplicate. Heating time of 3 minutes was found to be the optimum heating time giving the hydrogel with the most percentage swelling and was used for all syntheses.

1.5.2. Optimization of microwave oven power out-put for synthesis

The optimum microwave power out-put required for synthesis of the phosphoric acid SAH was determined by preparing the hydrogels under

different microwave oven power outputs of 140 – 700 watts (level 2–10 on the dial in the oven) and measuring their percentage swelling. The microwave power out-put that gave the product with highest percentage swelling was taken as the optimum power out-put. In a typical experiment, rice husk cellulose (2.00 g) was suspended in 30 mL of distilled water in a 200-mL beaker and treated with 10 mL phosphoric acid. The mixture was heated in a microwave oven at the lowest microwave oven power output i.e. 140 watts (level 2 on the dial in the oven) for 3 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 °C to a constant weight. The synthesis experiments were carried out in triplicate. This was repeated for the other microwave power outputs. Microwave oven power output of 420 watts (level 6 on the oven dial) was found to be the optimum heating oven power output and was used for all syntheses.

1.5.3. Optimization of amount of cross-linker (mL) used in synthesis

The optimum amount of cross-linker required for completion of the reaction was determined by reacting the rice husk cellulose with varied amount of phosphoric acid (i.e. 2, 4, 6, 8, 10, 12, and 14 mL) and measuring the percentage swelling of the isolated product. The amount of cross-linker that gave the product with highest percentage swelling was taken as the optimum amount required for complete crosslinking of the polymer chains. A typical synthesis involved reaction of 2.00 g of cellulose suspended in 30 mL of distilled water in a 200 mL beaker with a given amount of phosphoric acid under microwave heating at a power output of 420 watts for 3 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 °C to a constant weight. The experiments were carried out in triplicate. The optimum amount of cross-linker required for complete reactions was found to be 10 mL and was used for all syntheses.

1.6. Determination of the efficacy of the superabsorbent hydrogels

1.6.1. Planting conditions and application of superabsorbent hydrogel

The experiment was conducted in Darazo, Bauchi State, Nigeria in a greenhouse. The soils in the area are classified as sandy soils with low fertility and productivity (Maduakor, 1999). The experiment was laid out in randomized block design with three replications and six treatments (0, 1, 2, 3, 4 and 5 g of SAH). The soil samples were mixed with goat manure in the ration 1:3 (manure:soil) and transferred into black polythene bags (pots). The pots were saturated with borehole water for 2 days before planting. At planting, two DMRESR-Y maize variety seeds were gently pushed one inch into the soil in each of the pots. The pots were watered immediately after planting, and subsequently watered twice daily (morning and evening) until the seeds germinated (at 7 days). In order to improve the soil fertility, N. P. K. fertilizer with (20. 10. 10) formulation (Urea, diammonium phosphate, muriate of potash) was added after germination (14th day after planting). Varying amounts of the SAH (1, 2, 3, 4 and 5 g) was applied (on the 21st day) to the pots at a depth of 5 cm mixed with soil closer to the plant roots in triplicate. After application of the SAH, watering was done in the morning and again in the evening after which no more watering was done until harvest. The pot with soil without amendment of the SAH was considered as a control. Growth and yield parameters including plant height, the number of leaves, area of leaves, leaf length, leaf width were measured at weeks, 3, 6, 9 and 12, respectively to determine the effect of hydrogels. The mature and dry maize was harvested at week 12. The harvested maize cobs were dried on a mat. The yield attributes determined were number of cobs per pot, length of cobs, cob width, weight of cob, grain weight and number of grains were weighed on a digital analytical balance (grade).

1.7. Statistical analysis

The optimizations results obtained from the studies were subjected to analysis of variance (ANOVA) using minitab software version 17, Fisher least significance difference (LSD) test to generates mean at 5 % confidence level of significance.

2. Results and discussion

The objective of this study was to synthesize and characterize cellulose phosphate-based superabsorbent hydrogels (SAHs) from cellulose extracted from rice husks for use as a soil conditioner in arid and semi-arid agricultural zones. Accordingly, cellulose was extracted from rice husk and then crosslinked with phosphoric acid to form the SAHs. Results from characterization studies, as well as the efficacy of the SAHs in the growing of maize in a greenhouse, are presented and discussed in the present work

2.1. Extraction and characterization of Cellulose

Treatment of rice husks with of 80 % glacial acetic acid and 70 % nitric acid removed much of the lignin and hemicellulose from rice husk giving cellulose extract in 81.67 % yield. Fig. 3 shows a FT-IR spectrum of the rice husk cellulose extract.

The broad absorption band at 3432.39 cm^{-1} is attributed to the OH stretching vibrations [45]. The peak at 2924.13 cm^{-1} is due to C-H stretching vibration. The absorption band at 1631.81 cm^{-1} is due to the absorbed water while the band at 1384 cm^{-1} is characteristic for symmetric CH_2 bending vibrations. The hemicellulose and lignin peaks at 1508 and 1459 fully disappeared after extraction implying that they had been successfully removed. The band at 1104.55 cm^{-1} appeared due to the cellulose C-O-C stretching mode [19].

2.2. Optimizations condition for the synthesis of cellulose phosphate hydrogel

The optimal synthesis conditions of oven heating time, oven power out-put, and cross-linker to cellulose ratio for better super-absorbent hydrogels were investigated by varying one parameter and holding the others constant.

2.2.1. Heating time

Fig. 4 shows the variation of %swelling of hydrogels prepared at different microwave oven power output.

It is clear that the percentage swelling of the superabsorbents prepared reached its maximum of 853 % at 3 minutes of reaction time. This is in agreement with findings of Takigami et al. [42] who reported that the amount of crosslinking increases with an increase in incubation time. Longer heating times (beyond 3 minutes) did no lead to products with higher %swelling. On the contrary, the percentage swelling decreased from 853 % to 645 % at 5 minutes heating time. It is not clear to us yet why longer heating times give products with lower water absorbency.

2.2.2. Microwave oven power output

The optimum microwave oven power output was determined by preparing hydrogels under different power outputs from 2 to 10 (corresponding to 140 watts to 700 watts) using 2 g of cellulose, 3 minutes, and 10 mL of phosphoric acid (cross-linker). The results are summarized in Fig. 5.

It can be seen from the figure that as power output increased the percentage of swelling increased to a maximum of 877 % at 420 watts and decreased to 565 % at 700 watts power output. The power output of 420 watts was considered as optimum. At higher power out-put, hydrogen bond formation causes a tighter crosslinking network and leaves few voids for penetration of water, leading to a decrease in the

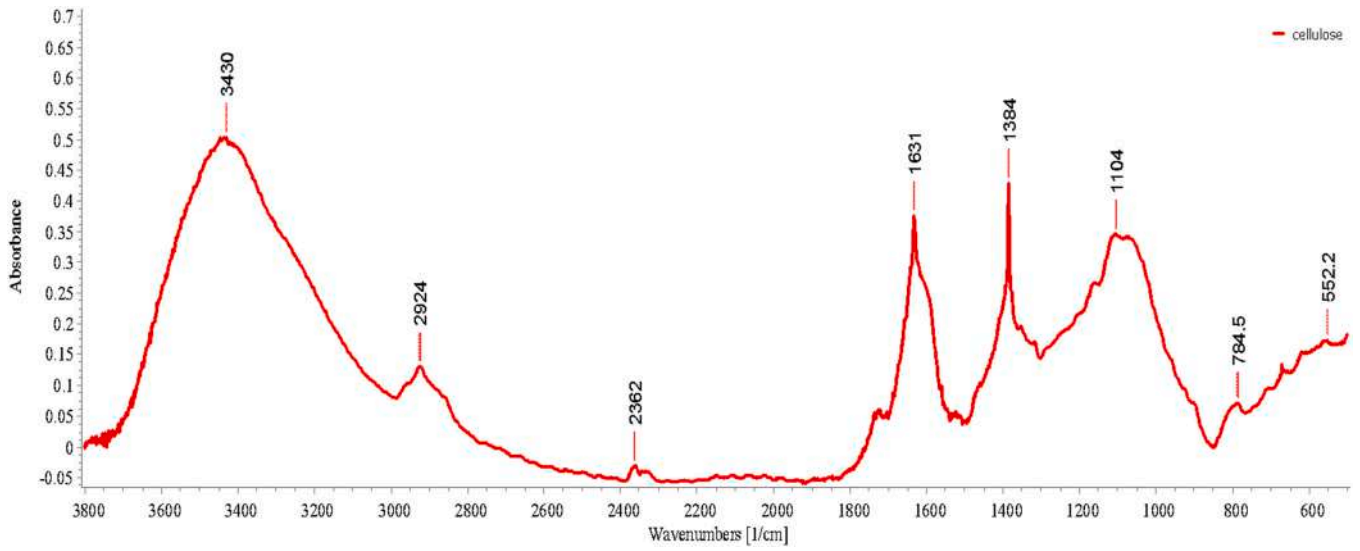


Fig. 3. FT-IR spectrum of extracted cellulose.

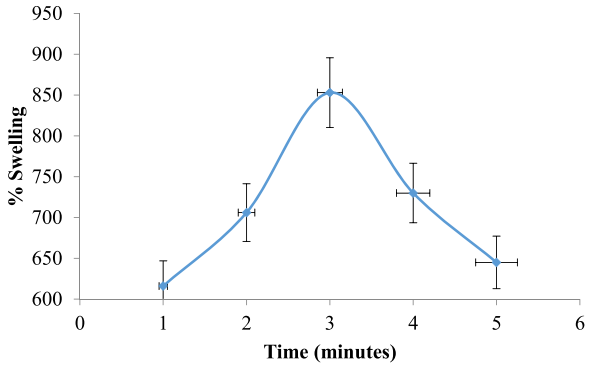


Fig. 4. Effects of heating time on percentage of swelling.

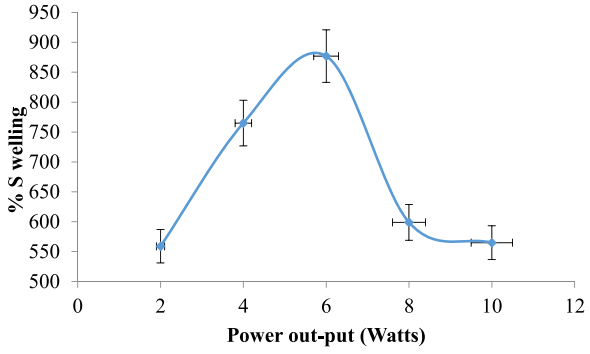


Fig. 5. Effects of power out on percentage swelling.

percentage swelling.

2.2.3. Amount of Cross linker (phosphoric acid)

The impact of cross linker (phosphoric acid) on the percentage of swelling was investigated at different amounts of cross linker ranging from 2 to 10 mL, using 2 g of cellulose, oven power output of 420 watts, and oven heating time of 3 minutes. The percentage of swelling increased from 744 % at 2 mL of phosphoric acid to 860 % at 10 mL of phosphoric acid. An adequate amount of phosphoric acid leads to effective crosslinking between the hydroxyl group of cellulose and the phosphate group leading to the formation of a superabsorbent hydrogel. Xiao et al. [47] revealed that a high degree of cross linker in the polymer network reduces the percentage of swelling because water molecules find it difficult to penetrate.

2.3. Synthesis and characterization of cellulose cross-linked with phosphoric acid

When cellulose suspended in distilled water was treatment with 10 mL of 85 % phosphoric acid and heated in a microwave oven at a power output of 420 watts for 3 minutes, the phosphate-crosslinked cellulose was achieved. Fig. 7 shows a FTIR spectrum of the resultant product.

The absorption band which appears at 2380.62 cm^{-1} is attributed to the formation of P-H bond [39]. The sharp band at 1350.77 cm^{-1} was due to P═O bond stretching mode [15] while the peak at 886.80 cm^{-1} corresponds to P-O stretching in phosphate ester [39]. These bands confirm the presence of the phosphate moiety in the cellulose. The elemental composition of rice husk, cellulose and phosphate crosslinked cellulose was determined by X-ray fluorescence (XRF) spectroscopy. The results are summarized in Table 1. It is clear from the results that phosphate crosslinked cellulose contained a much higher percentage of P_2O_5 (0.483 %) than the 0.183 observed in the parent cellulose. The percentage of silica in rice husk is low because it contains some metal oxide (impurities) as compared to the amount of silica in the extracted cellulose.

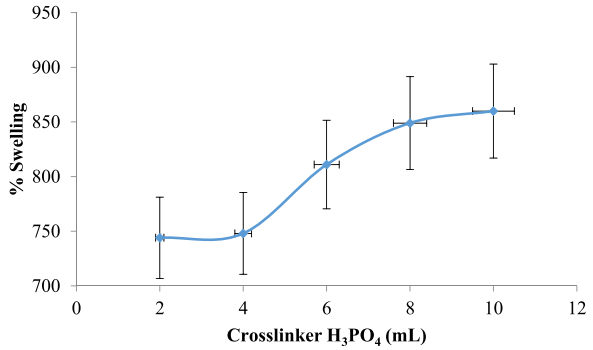


Fig. 6. Effect of cross-linker amount on percentage swelling.

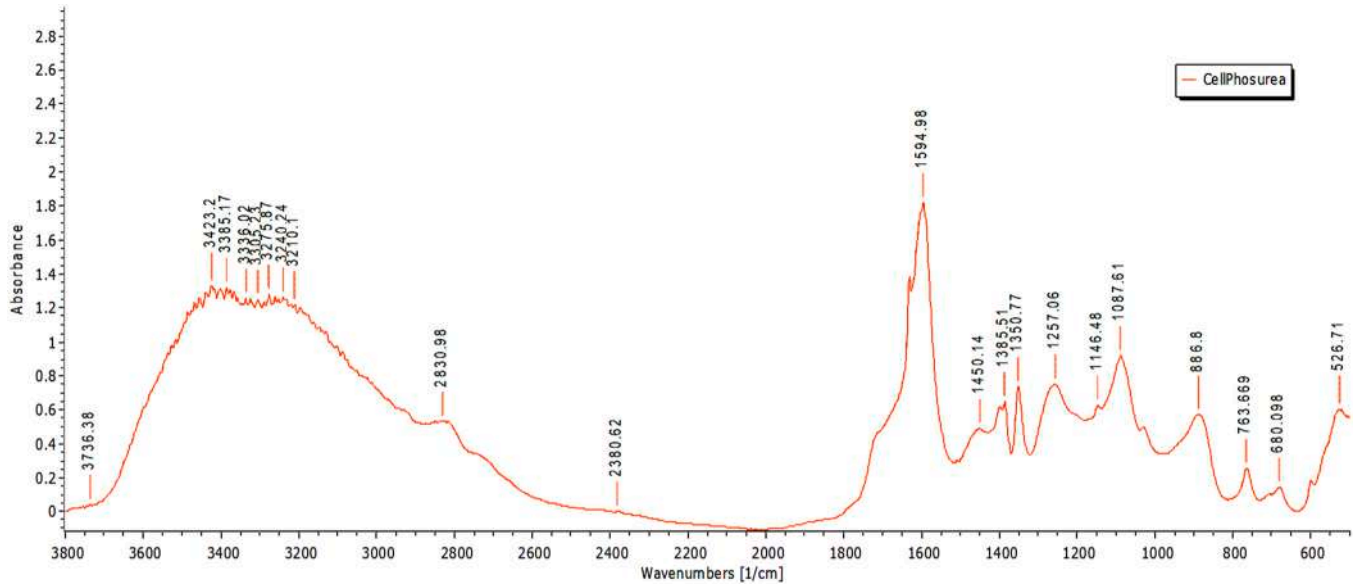


Fig. 7. FTIR of cellulose cross-linked with phosphoric acid.

Table 1
Elemental composition of rice husk cellulose, and cellulose crosslinked with phosphoric acid by XRF analysis.

Elemental component	Rice husk (%)	Cellulose (%)	Cellulose crosslinked with H_3PO_4 (%)
Al_2O_3	0.30	0.152	0.293
SiO_2	72.1	98.834	95.920
P_2O_5	0.06	0.183	0.483
S		0.133	0.244
Cl		0.203	0.167
K_2O	0.72	0.099	0.965
CaO	0.43	0.154	1.273
Ti	0.05	0.062	0.139
Cr		0.008	0.017
Mn	0.15	0.029	0.155
Fe	0.15	0.135	0.311

2.4. X-ray diffraction of superabsorbent hydrogels

The rice husk cellulose and its phosphoric acid cross-linked derivative were subjected to powder x-ray diffraction studies. The XRD patterns (see Fig. 8) showed the characteristic peak at $2\theta = 22^{\circ}$. However, there was a remarkable decrease in the broad peak intensity between 20 and 24°θ in the phosphate crosslinked cellulose relative to the parent cellulose. A similar result was reported by Wan Rosli et al., [44] in which it as noted that that the backbone of cellulose was disrupted after phosphoration and cellulose crystallinity reduced. It has also been reported that the functionalization of cellulose diminishes its crystallinity [15,39].

2.5. Scanning electron microscopy of rice husk cellulose

The figure above shows the scanning electron microscopy (SEM) image of extracted rice husk cellulose at 5.00 kx magnification. The image shows a rough and rigid structure. This could be attributed to the removal of lignin, hemicellulose and other impurities (metallic oxides) found in rice husks. As shown on the surface morphology, the white colour also confirms the removal of the non-cellulosic materials, which was also confirmed by the FT-IR spectroscopy. Aydin et al. [8] reported that the removal of the non-cellulosic materials led to the distortion of the cellulose fibrils.

2.6. Efficacy of superabsorbent hydrogels (SAH) on maize growing

To evaluate the efficacy of the superabsorbent hydrogel on maize growing, the pot soils on which maize plants planted were treated with variable amounts of SAH, and the growth parameters monitored regularly for twelve weeks. It is important to note that watering was done for the first 21 days after planting and discontinued to mirror the situation in arid and semi-arid regions where rains sometimes fail as soon as crops germinate.

2.6.1. Plant height

The heights of plants planted with the Super-Absorbent Hydrogels were measured at weeks 3, 6, 9 and 12 after planting. The mean heights of maize plants grown with varying amounts of SAH, that is, 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g were found to be 29.53±0.70, 28.76 ±0.49, 28.95±0.67, 29.55±0.88, 28.90±0.98 and 29.50±0.67 cm respectively, at week 3. There was no significant variation in plant heights in all pots ($p > 0.05$) (See Table 2). The mean heights increased to 42.94±0.08, 192.81±0.08, 204.59±1.20, 214.13±1.06, 224.20 ±1.63 and 232.96±1.85 cm, respectively at 12 week.

Statistically, the increase in the plant heights was significantly different for the different hydrogel doses (0 (control), 1.00, 2.00, 3.00, 4.00, and 5.00 g) as indicated in Table 2. The increase in plant height is attributable to the continued availability of water to plants throughout the growth period due to the retention and slow release by the hydrogel even in the absence of regular watering. Al-Harbi et al. [3] and Sendur Kumaran et al., [36], reported similar results in tomatoes and cucumber, respectively. The crops that were grown without the hydrogel died off at week 12. Yang et al. [49] have also reported that drought stress significantly affected plant height.

2.6.2. Number of leaves

The mean number of leaves per plant were determined for plants grown under varying hydrogel amounts, that is, 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g at weeks 3, 6, 9 and 12 after planting. The results are summarized in Table 2 but the trends can be seen more clearly displayed in Fig. 10, below.

As shown in Fig. 10, the mean number of leaves of a maize plant at various amounts of the SAH that is 0 (control), 1, 2, 3, 4, and 5 g were found to be 4.00±1.00, 4.66±0.15, 4.33±0.57, 4.00±1.00, 4.33±0.57, 5.00±1.00 respectively at week 3. The mean numbers of leaves for all plants were not significantly different ($p > 0.05$) as shown in Table 2. At

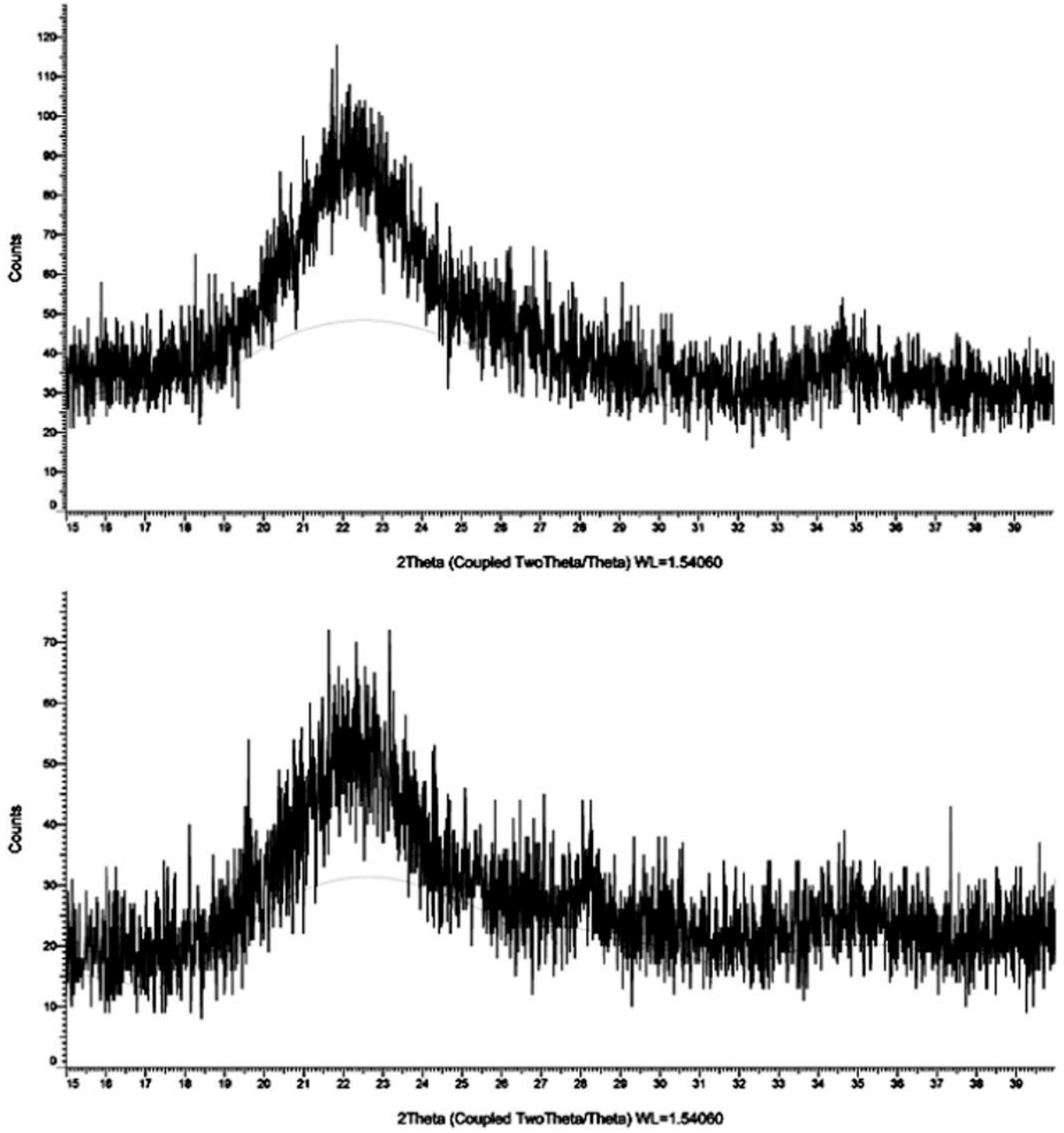


Fig. 8. X-ray patterns of rice husk cellulose (top) and rice husk cellulose crosslinked with phosphoric acid (bottom).

week 12, the numbers of leaves numbers increased to 6.00±1.00, 8.00 ±1.00, 9.66±1.15, 10.00±1.00, 11.00±1.00, and 12.66±1.52 in plants grown pots with soils treated with 0 (control), 1, 2, 3, 4 and 5 g of hydrogels, respectively. The number of Leaves in plants grown soils treated with 4 and 5 g of hydrogels were not significantly different ($p > 0.05$) while those with 0, 1, 2, and 3 g were significantly different ($p < 0.05$) at week 12. This is not unexpected since having higher doses of SAH meant that more water was available to the plants during the days watering was avoided. Al-Harbi et al. [3] and Sendur Kumaran et al., [36] observed similar results.

2.6.3. Leaf length (cm)

The mean leaf length of maize plants treated with 0 (control), 1, 2, 3, 4, and 5 g of hydrogels, were measured at week 3, 6, 9, and 12 after planting and the results are as shown in Fig. 10 below. It can be seen from the figure that maximum leaf length values were attained in the 12th week.

At week 3, before the application of the hydrogel, the mean Leaf length of maize plants grown by varying SAH amounts of hydrogel 0 (Control), 1, 2, 3, 4 and 5 g were found to be 28.69±0.68, 27.09±2.93, 27.94±2.54, 28.36±0.73, 31.33±1.94 and 31.75±1.27 respectively. The leaf lengths of all plants in all pots were not significantly different

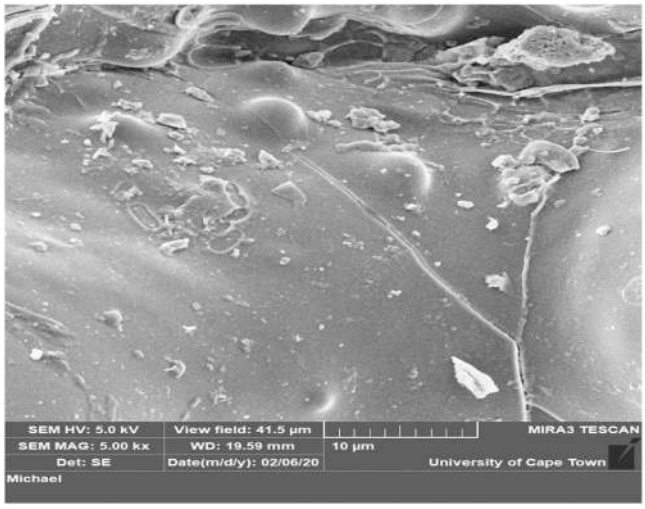


Fig. 9. Scanning electron micrograph of rice husk cellulose.

(p>0.05). By the 12th week, the mean leaf lengths increased to 33.40 ±1.73, 66.46±0.73, 68.58±0.00, 71.12±0.00, 73.66±1.27, and 75.35 ±1.46 respectively. The leaf lengths of plants under the 4 and 5 g treatments were not significantly different ($p > 0.05$) while those with 0, 1, 2, and 3 g were significantly different ($p < 0.05$) at week 12, as referred in Table 2.

At week 3, there was no significant difference ($p > 0.05$) in the leaf lengths of the maize in all experimental pots possible reflecting similarity of soils in the pots. The leaf length varied significantly as the dosage of the SAH increased. The leaf lengths in plants grown in control pots were significantly different ($p < 0.05$) from those of plants grown in hydrogel treated soils. Plants grown in pots with soils treated with 5 g of hydrogel recorded the highest values of leaf lengths.

2.6.4. Leave width (cm)

The mean leaf widths were determined at week 3, 6, 9 and 12 after maize planting under varying amounts of the hydrogel dose (0, 1, 2, 3, 4 and 5 g). The results are summarized in Fig. 12.

It can be seen from Fig. 12, that the mean leaf width of maize plants at the start at week 3 after planting were 2.28±0.00, 2.28±0.25, 2.70 ±0.38, 2.96±0.38, 3.63±0.15 and 3.46±0.14 cm for the pots labeled 0 (control), 1, 2, 3, 4 and 5 g, respectively. The mean leaf widths were not significantly different as was expected ($p > 0.05$). At week 12, the mean leaf width increased to 2.69±0.02, 4.31±0.00, 4.56±0.25, 4.56 ±0.25, 5.41±0.14 and 5.66±0.15 for treatments with 0 (control), 1, 2,

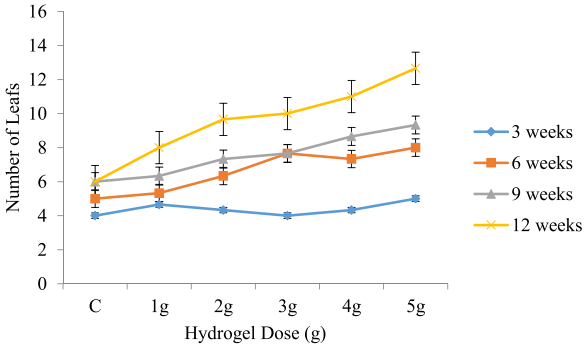


Fig. 10. Variation of number of leaves in plants grown with phosphoric acid SAH.

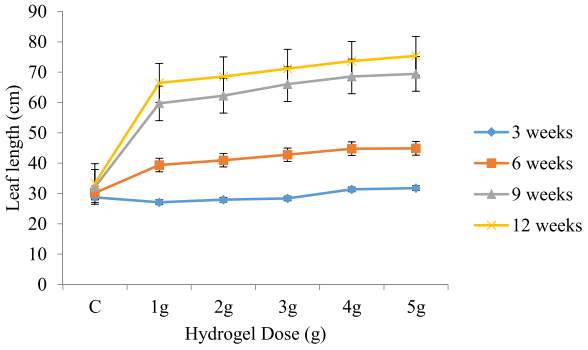


Fig. 11. Variation of leaf length in maize plants treated with phosphoric acid SAH, C is control experiment.

Table 2
Effect of SAHs crosslinked with phosphoric acid on pre-harvest studies.

Weeks	SAH Dose	(Plant Height) Mean±SD	(Number of Leaves) Mean±SD	(Leaf Length) Mean±SD	(Leaf Width) Mean±SD	(Leaf area) Mean±SD
3	Control	29.53±0.70^{a}	4.00±1.00^{a}	28.69±0.68^{a}	2.28±0.00^{b}	48.03±1.91^{b}
	1 g	28.76±0.49^{a}	4.66±0.15^{a}	27.09±2.93^{a}	2.28±0.25^{b}	46.77±1.08^{b}
	2 g	28.95±0.67^{a}	4.33±0.57^{a}	27.94±2.54^{a}	2.70±0.38^{b}	56.61±8.08^{b}
	3 g	29.55±0.88^{a}	4.00±1.00^{a}	28.36±0.73^{a}	2.96±0.38^{ab}	62.90±6.83^{b}
	4 g	28.90±0.98^{a}	4.33±0.57^{a}	31.33±1.94^{a}	3.63±0.15^{a}	85.56±6.77^{a}
	5 g	29.50±0.67^{a}	5.00±1.00^{a}	31.75±1.27^{a}	3.46±0.14^{a}	82.74±6.51^{a}
6	Control	38.93±0.35 ^{f}	5.00±1.00^{d}	30.18±0.20^{d}	2.55±0.03^{c}	58.57±0.46^{d}
	1 g	52.43±0.11^{e}	5.33±0.57^{d}	39.37±1.27^{c}	3.46±0.14^{b}	102.57±7.32^{c}
	2 g	61.34±1.32^{d}	6.33±0.57 ^{cd}	40.97±0.57^{bc}	3.55±0.00^{b}	109.51±1.96^{bc}
	3 g	68.79±0.88^{c}	7.66±0.15^{bc}	42.75±0.73^{ab}	3.80±0.25^{ab}	122.24±9.99^{abc}
	4 g	78.16±0.61^{b}	7.33±0.57^{ab}	44.02±0.73^{a}	3.80±0.25^{ab}	125.88±9.25^{ab}
	5 g	83.25±0.17^{a}	8.00±1.00^{a}	44.87±1.46^{a}	4.22±0.14a	142.58±9.50^{a}
9	Control	41.83±0.25 ^{f}	6.00±1.00^{b}	32.17±0.05^{e}	2.69±0.01^{b}	60.41±1.03^{d}
	1 g	126.20±1.16^{e}	6.33±0.57^{b}	59.69±1.27^{d}	5.07±0.25^{a}	227.58±16.21^{c}
	2 g	134.25±1.37^{d}	7.33±0.57^{a}	62.23±1.27^{c}	5.51±0.31^{a}	252.98±11.66^{bc}
	3 g	143.11±1.02^{c}	7.66±1.52^{a}	66.04±0.00^{b}	5.58±0.25^{a}	176.77±12.58^{ab}
	4 g	154.65±0.97^{b}	8.66±1.52^{a}	68.58±0.00^{a}	5.58±0.25^{a}	287.41±13.07^{a}
	5 g	163.69±0.84^{a}	9.33±0.57^{a}	69.42±0.73^{a}	5.66±0.15^{a}	295.40±9.59^{a}
12	Control	42.94±0.08 ^{f}	6.00±1.00^{d}	33.40±1.73^{a}	2.69±0.02^{c}	61.62±0.57^{c}
	1 g	192.81±1.75^{e}	8.00±1.00^{c}	66.46±0.73^{a}	4.31±0.00^{b}	215.24±2.37^{b}
	2 g	204.59±1.20^{d}	9.66±1.15^{bc}	68.58±0.00^{a}	4.56±0.25^{b}	235.16±13.07^{b}
	3 g	214.13±1.06^{c}	10.00±1.00^{ab}	71.12±0.00^{a}	4.56±0.25^{b}	243.87±13.55^{b}
	4 g	224.20±1.63^{b}	11.00±1.00^{a}	73.66±1.27^{a}	5.41±0.14^{a}	294.80±19.10^{a}
	5 g	232.96±1.85^{a}	12.66±1.52^{a}	75.35±1.46^{a}	5.66±0.15^{a}	320.64±12.63^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

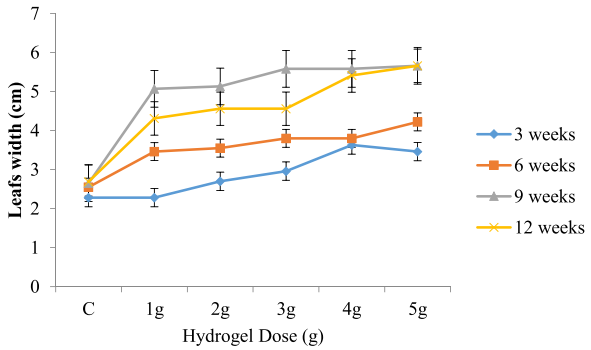


Fig. 12. Variation of leaf width in plants treated with phosphoric acid SAH.

3, 4 and 5 g respectively. The mean leaf widths in plants treated with 1 and 2 g of hydrogel, respectively, were not significantly different while those treated with 3, 4, and 5 g of hydrogel were significantly different ($p < 0.05$) at week 12. This implies that at a high dosage of the hydrogels, the plants experienced less drought stress because the hydrogel continued to supply water to the plant, even when watering was discontinued. It has been reported elsewhere that the most prominent growth as indicated by leaf diameter, the height of the plant, and number of leaves was observed in soils treated with hydrogel as compared to the control [5].

2.6.5. Leaf area (cm)

The variation of leaf area in maize plants was investigated in maize planted with 0 (control), 1, 2, 3, 4 and 5 g of hydrogel while keeping the other parameters constant and the results are displayed in Fig. 13.

The mean leaf area of maize plants grown under varying SAH amounts of 0 (control), 1, 2, 3, 4 and 5 g were found to be 48.03±1.91, 46.77.±1.08, 56.61±8.08, 62.90±6.83, 85.56±6.77 and 82.74 ±6.51 cm, respectively at week 3. The mean leaf areas increased to 61.62±0.57, 215.24±2.37, 235.16±13.07, 243.87±13.55, 294.80 ±19.10 and 320.64±12.63 cm for plants treated with 0 (control), 1, 2, 3, 4 and 5 g of hydrogels, respectively. The leaf areas of plants treated with 4 and 5 g of hydrogels were not significantly different while those with 0, 1, 2 and 3 g were significantly different ($p < 0.05$) at week 12. Plant growth, productivity and health are related to leaf area, being an aerial part of the plant playing a vital role in the photosynthetic capacity through light absorbing pigments. Leaf area was seen to increase with the amount of SAH. This is probably related to increased availability of water to plants which in turn influences the amount of minerals and other nutrients available to the plants [3,50]. In this way the water holding capacity of SAH influences the leaf area of maize.

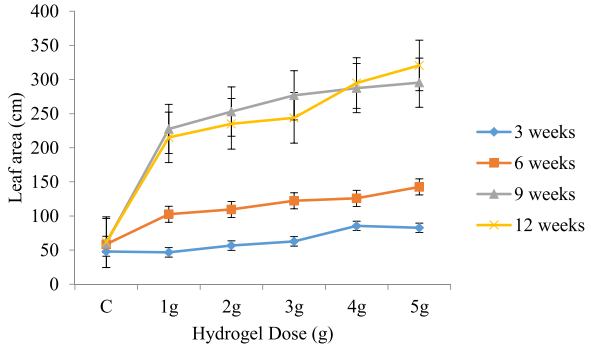


Fig. 13. Variation of leaf area in maize plants treated with phosphoric acid SAH.

2.7. Evaluation of post-harvest parameters

The yield parameters measured included the number of cobs per plant, length of cob, cob width, weight of cob, grain weight and number of grains per cob. The results are presented in Fig. 14 below.

2.7.1. Number of maize cobs, cob length and Cob width

The variation of the number of cobs per plant was determined for plants grown in soils treated with different hydrogel doses, namely, 0 (control), 1, 2, 3, 4, and 5 g. The mean number of cobs increased from 0.00 to 2.33. Similar results have been reported in other studies [20].

The mean cob length increased from 0.00 to 13.79 cm in the plants treated with the phosphoric acid SAH. The cob length was significantly higher in the plants grown in pots treated with high doses (4 and 5 g) than cobs in plants grown in pots treated with 1, 2, or 3 of SAH (see Table 3). Similar cob lengths were also reported by Niazuddin et al. [30] and Hossain [14]. Kumar [20] observed that the application of 150 % SAH to soil had a significant effect on cob length.

The mean cob width increased from 0.00 to 3.36 cm in plants treated with phosphoric acid SAH. The results obtained show that the cob width increased with an increase in hydrogel dose. The highest value of the cob width was observed in plants grown with 5 g of SAH.

2.7.2. Cob weight, number of grains and grain weight

The mean cob weight observed varied from 0.00 to 107.33 g with cob weight was observed for plants grown in pots with soils treated 5 g SAH (see Table 3). The number of grains per maize cob followed a similar trend as the cob weight. In a similar kind of study, Khadem et al., [17] observed that the application of superabsorbent hydrogels to soil increased the number of grains by 16.2 %. In this study, the highest number of grains was observed in maize plants grown with 5 g of hydrogel.

The mean grain weight increased from 0.00 in plants grown without SAH to 84.00 g for plants planted in soils treated with SAH. The grain weight of plants grown at 5 g gave the highest grain weight (see Table 3). It has been reported that the application of superabsorbent hydrogel enhanced the 100 seed weight of sunflower as compared to the zero (control) [29].

3. Conclusions

The study successfully synthesized a cellulose phosphate-based superabsorbent hydrogel (SAH) from rice husks cellulose using microwave heating. The hydrogel was characterized by FT-IR spectroscopy, X-ray diffraction and X-ray fluorescence. The hydrogel synthesis conditions, namely, microwave heating time, microwave oven power output, and amount of cross-linker utilized were optimized by observing their influence on the percentage swelling of the hydrogel prepared. The hydrogel with optimal percentage swelling of 877 % was found only possible under ideal synthesis condition of 3 minutes microwave heating

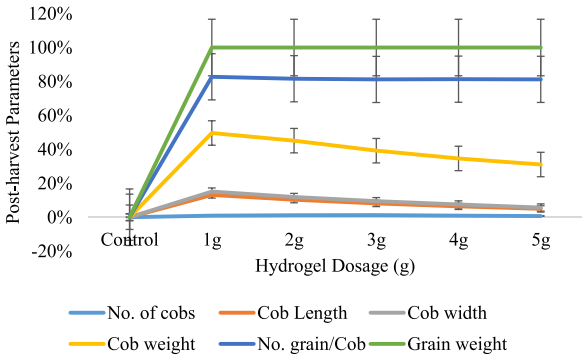


Fig. 14. Variation of post-harvest parameters with hydrogel dosage.

Table 3
Effect of SAHs crosslinked with phosphoric acid on post-harvest studies.

SAH Dose	Number of Cobs Mean ±SD	Cob Length Mean ±SD	Cob width Mean ±SD	Cob weight Mean ±SD	No. of grain per cob Mean ±SD	Grain weight Mean ±SD
Control	0.00±00^{c}	0.00 ±0.00^{e}	0.00 ±0.00^{f}	0.00 ±0.00^{f}	0.00 ±0.00^{f}	0.00 ±0.00^{f}
1 g	0.66 ±0.57^{bc}	8.72 ±0.16^{d}	1.42 ±0.03^{e}	24.67 ±5.51^{e}	23.67 ±4.73^{e}	12.33 ±2.52^{e}
2 g	1.33 ±0.57^{ab}	10.30 ±0.15^{c}	1.75 ±0.21^{d}	37.33 ±3.21^{d}	41.00 ±3.00^{d}	20.67 ±2.08^{d}
3 g	2.00 ±0.00^{a}	11.08 ±0.46^{bc}	2.14 ±0.57^{c}	48.00 ±1.73^{c}	67.67 ±3.51^{c}	30.33 ±2.52^{c}
4 g	2.00 ±0.00^{a}	12.10 ±0.22^{b}	2.40 ±0.02^{b}	59.67 ±4.04^{b}	102.67 ±5.69^{b}	41.00 ±2.65^{b}
5 g	2.33 ±0.57^{a}	13.79 ±0.95^{a}	2.67 ±0.08^{a}	83.33 ±1.58^{a}	165.00 ±9.17^{a}	61.67 ±3.06^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

time, power output of 420 watts (level 6 on the microwave oven control dial), 10 mL of cross-linker (phosphoric acid). The use of microwave heating has the advantage of reducing cost, through saving energy, and ease of handling. The superabsorbent hydrogel prepared was found to be efficacious in maize growing in a greenhouse as determined by plant growth and yield parameters measured. These were found to be significantly influenced by the dose of SAH. The highest parameters were recorded at 5.00 g SAH dose.

CRediT authorship contribution statement

Adamu Abdulhameed: Conducted the data collection, drafted the initial manuscript and performed the statistical analyses. **Harun Mbuvi**: Was the research supervisor who, conceived the study, designed the experiments and coordinated the research project. **Evans Changamu**: Research co-supervisor, coordinated the research project, contributed to the interpretation of data and provided critical revisions to the manuscript. **Irene Githinji**: Assisted in data collection and contributed to edit the manuscript. **Francis Maingi**: Assisted with data analysis and contributed to manuscript editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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