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Preparation of low-cost and eco-friendly superabsorbent based from rice husk cellulose cross-linked with boric acid using microwave

Abstract

Superabsorbents are polymers capable of absorbing and retaining high amount of water. It is widely used in disposal diapers, agriculture, water purification and biomedical among others. Majority of the superabsorbents reported in literature are acrylate based material, hence they are not degradable. This work focused on the synthesis of low-cost and eco-friendly superabsorbent from cellulose cross-linked with boric acid through microwave irradiation and conventional reflux method. Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) were carried out in order to confirm the formation of intermolecular bond between hydroxyl group and boric acid. The microwave irradiation was found to be more effective in the process of cross-linking than the other conventional methods. The Optimum conditions of power, time and amount of cross-linker required for the production of most desirable, stable and high water absorptivity were investigated, the optimum swelling capacity was found to be 986%. (at 3 minutes, power output 6 equivalent to 420watt, 1.0g of boric acid).

Keywords: boric acid, cellulose, crosslinking, superabsorbent hydrogel, microwave

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Adamu Abdulhameed,[1] Harun M Mbuvi,[2] Evans O Changamu,[2] Francis M Maingi[3]
[1]Chemistry Department, Bauchi State University, Nigeria
[2]Chemistry Department, Kenyatta University Nairobi, Kenya
[3]Science Technology and Engineering Department, Kibabii University, Bungoma, Kenya

Correspondence: Adamu Abdulhameed, Chemistry Department, Bauchi State University, Gadau, Nigeria, Tel +2348033726927, Email adamhameed1@gmail.com

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Introduction

Cellulose is the most abundant natural polymer on earth. It is linear, long-chain, water-insoluble, inexhaustible, biocompatible, degradable and environmentally friendly. Being polysaccharide, it is formed as a result of repeating unit of D-glucose, linked by glycosidic bond β (1-4). Cellulose is capable of absorbing water due to the presence of hydroxyl group,[1] and can be further modified.[2] Cellulose unit has three hydroxyl groups (C2, C3 and C6) which are highly polar and reactive.[3]

Cellulose has been isolated from several agricultural wastes such as, orange peels[4] palms oil,[5] banana,[6] cotton waste,[7] rice husk,[8] durian[9] and sago waste.[10] To a great extent, rice husk is being considered as an agricultural waste material which is burnt thereby contaminating the environment. This becomes a very big challenge to scientist to explore ways of making them valuable. Literature has shown that the organic aspect of rice husk contains cellulose, hemicellulose and lignin. In this study, cellulose was isolated from rice husk based on its advantage properties, which include biodegradability, biocompatibility and availability.[11]

Superabsorbents are polymers capable of absorbing and retaining water up to 1500 times of their original weight. The superabsorbents containing the retained water are known as hydrogel.[12] The ability of the water absorbency is due to the presence of hydrophilic groups on the polymer chain, such as OH, COOH, CONH, $CONH_2$ and SO_3H.[13] They are also reported to be sensitive to ionic strength and pH of the solution.

Superabsorbent hydrogels are widely used in various fields such as hygiene napkins, disposal diapers, soil for horticulture and agriculture, water purification, food, construction and building, biomedical application and controlled release.[14] Nowadays, researchers have focused on development of hydrogels for tissue engineering,[15] sensor[16] and drug delivery.[17] The principal raw materials used in making superabsorbents are petroleum based products, such as acrylonitrile, acrylic acid (AA) and acrylamide. They were restricted from use due to being non-degradable, non- renewable and environmentally unfriendly. With idea of green chemistry, scientists are now focusing on developing biodegradable materials in place of petrochemical products which can equally serve same purpose.

Several studies have been done on synthesis of cellulose based superabsorbent hydrogel by using carboxymethylcellulose cross-linked carbodiimide[18] and divinylsulphone,[19] esterification has also been achieved by using formaldehyde based products.[20] However, these cross-linkers were reported to be toxic, expensive and unavailable. Boric acid was tested and reported to be good and environmentally friendly. Boron is one of the essential elements required for plant growth; it is often toxic at high concentration. Borax is a mineral found in ground and known to be environmentally friendly, it is capable of crosslinking molecules containing diol in aqueous solution under alkaline condition thereby forming borate complex.

Literature has shown that, there is a strong bond interaction existing between boric acid and hydroxyl group, the empty p orbital of boron, in boric acid is electrophilic in nature, as a result it react rapidly with other nucleophiles thereby forming a complex.[21] Cellulose have several hydroxyl group, it is therefore expected that boric acid can crosslink them as shown in the Figure 1.

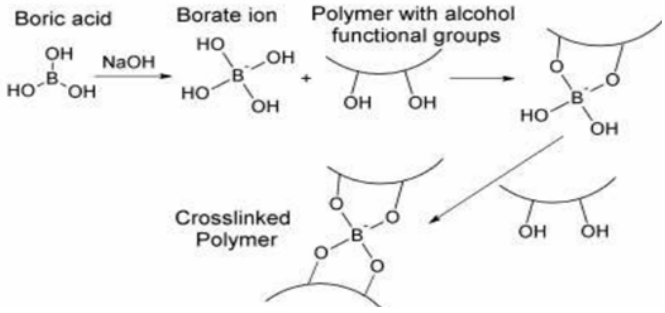

Figure 1 Cross-linking of Boric acid and available OH groups (Ref).

Liu et al.,[22] crosslinked poly(vinyl alcohol) with borax and hydrolyzing PVAc thereby forming a gel.[23] examined the structural and rheological features of poly(vinyl alcohol)/borate hydrogel, and was further used by[24] for cleaning painted surfaces.

Reflux (using a hot plate) method of heating is attained by several hours of heating, microwave irradiation is an alternate source of energy, which is considered a more efficient method of heating for a chemical reactions. Microwave increases the rate of chemical reaction through the thermal effect. Mazzocchia et al.[25] reported that microwave irradiation fastens conversion and chemical reaction rate.

Several studies have been done on crosslinking of cellulose (hardwood Kraft) but there is limited information on using rice husk to crosslinked with boric acid. Therefore, the aim of this study is to synthesized a superabsorbent hydrogel from rice husk crosslinked with boric acid, optimized the condition for synthesis using a microwave.

Materials and methods

Materials

The rice husk was sampled from Euro rice mills in Mwea, Kirinyaga County–Kenya. Glacial acetic acid was purchased sfrom Merck Chemical Co. (Darmstadt, Germany). Nitric acid, boric acid, (Oil bath) heating mantle, 250mL round bottom flask, retort stand, condenser and ramtons microwave (RM 240).

Methods

Extraction of cellulose

About 5.00g of rice husk was placed in a 250mL Erlenmeyer flask and 100mL of 80% glacial acetic acid, 10mL of 70% nitric acid were added. The flask was covered using aluminium foil and heated in an oven at 120ºC for 20 minutes. The sample mixture was allowed to cool and 60mL of distilled water was added. The mixture was filtered and washed with distilled water and then with 95% ethanol. The residue was dried in an oven at 60°C for 19hrs (Plate 1).[26]

Plate 1 Extracted cellulose from rice husk

The extract yield of cellulose was calculated using equation 1

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

Synthesis of Superabsorbent hydrogel

Synthesis SAH by cross-linking cellulose with boric acid under microwave heating

About 2.00g of extracted cellulose was added to 30mL of distilled water in a 200mL beaker. The contents of the beaker were stirred at room temperature for 24 hours during which all the material dissolved. The resulting solution was treated with 1.0g of boric acid and heated in a microwave oven at a power output of 280watts for 5 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 40ºC to constant weight. The product was characterized by determining percentage swelling, FT-IR spectroscopy, XRD.

Synthesis of SAH by crosslinking cellulose with boric acid under reflux

About 2.00g of extracted cellulose was added to 30mL of distilled water in a 200mL beaker. The contents of the beaker were stirred at room temperature for 24 hours during which all the material dissolved. The solution was transferred into a round- bottomed flask after reflux set-up and 1.0g of boric acid was added and heated at 80°C for 12 and 24 hours. 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 40ºC until it maintained a constant weight. The product was subjected to FT-IR spectroscopy.

Swelling ratio

The equilibrium swelling capacity was measured by weighing the sample before and after immersion in distilled water for 24hrs followed by removal of the excess water on the surface with a syringe and filter paper. The swelling ratio was obtained using the equation 2:

$$\%Swelling\ (\%\,\mathrm{S}) = 100\left(\frac{m_t - m_o}{m_o}\right) \qquad (2)$$

Where m_t is the initial weight and m_o is the final mass of the hydrogel.

Characterisation

Fourier Transform Infrared (FTIR)

FT-IR was used to identify the functional groups in cellulose and the SAHs prepared. About 1.0mg of dried samples was mixed with 25mg of KBr and made into a pellet. The Fourier transform infrared spectra were recorded on a Shimadzu IR Tracer -100 spectrophotometer in the mid-IR region of 3800-400cm^{-1}.

X-ray Diffraction (XRD)

The diffraction patterns of the extracted cellulose and cellulose cross-linked with boric acid were recorded on a D2 PHASER Bruker AXS X-ray diffractometer. A hot air oven was used to dry the powder samples at 105°C for 3 hours before testing. The scattering angle (2θ) ranged from 10 to 60° at a scan rate of 5°/min.

Optimization condition for synthesis

Optimization of reaction time

To determine the optimum condition for completion of the reaction, the boric acid SAH was prepared under varied reaction times i.e 1–5 minutes while other conditions were kept constant and the percentage swelling of each product was determined. The reaction time that gave the product with the highest percentage of swelling was taken as the optimum reaction time. In a typical synthesis, 2.00g of cellulose was added to 30mL of distilled water into a 200mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 1.00g boric acid and heated in a microwave at a power output of 280watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, and then dried in an oven at 40°C to a constant weight.

Optimization of microwave power out-put for synthesis

To determine the optimum microwave power out-put required for the synthesis of the boric acid SAH, the percentage swelling of

the product prepared under varied microwave power output i.e 2–10 while other conditions were kept constant and the percentage swelling of each product were determined. The microwave power output that gave the product with the highest percentage of swelling was taken as the optimum reaction time. In a typical synthesis, 2.00g of cellulose was added to 30mL of distilled water into a 200mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 1.0g boric acid and heated in a microwave at a power output of 140watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, and then dried in an oven at 40°C to a constant weight. The experiments were carried out in triplicates.

Optimization of amount of crosslinker (g) used in synthesis

To determine the optimum amount of crosslinker for completion of the reaction, the boric acid SAH was prepared under the varied amount of crosslinker i.e 0.5, 0.6, 0.7, 0.8, 1.0, 1.1, and 1.2 boric acid while other conditions were kept constant and percentage swelling of each product was determined. The amount of crosslinker that gave the product with the highest percentage of swelling was taken as the optimum. In a typical synthesis, 2.00g of cellulose was added to 30mL of distilled water into a 200mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 2mL phosphoric acid and heated in a microwave at a power output of 280watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled waterand then dried in an oven at 40°C to a constant weight. The experiments were carried out in triplicates.

Results and discussion

The percentage yield of cellulose

In the process of removal of lignin and hemicellulose, from rice husk cellulose that had been obtained was then characterized to determine the amount of α-cellulose (Plate 1) content using equation 1 above. The result of the cellulose content from rice husk is in the amount of 81.67% (Figure 2) (Figure 3).

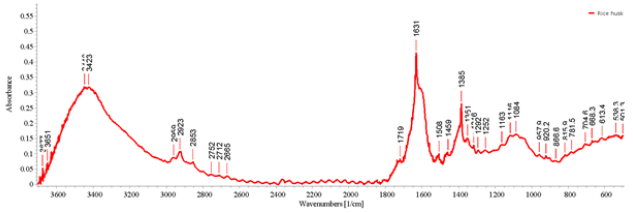

Figure 2 FT-IR spectrum of rice husk.

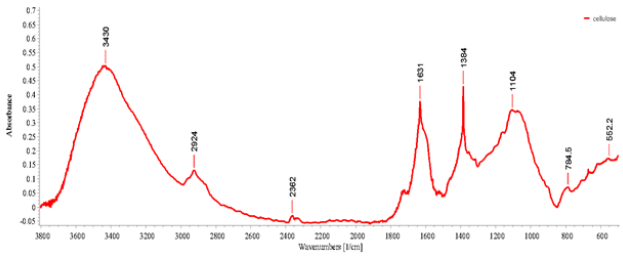

Figure 3 FT-IR spectrum of cellulose.

The figure above represents the FT-IR of cellulose. The broad absorption band at 3432.39cm^{-1} is a feature of the presence of OH stretching vibrations and revealed the formation of hydrogen bonds and intramolecular and intermolecular hydrogen bonds.[27] The peak at 2924.13cm^{-1} is due to C-H stretching vibration. The absorption band at 1631.81cm^{-1} is the absorbed water, the band at 1383.95cm^{-1} is a characteristic of symmetric CH_2 bending vibrations. The hemicellulose and lignin peaks at 1508 and 1459 fully disappeared after extraction as shown in Figure 1. The band at 1104.55cm^{-1} appears due to C-O-C stretching.[28] Therefore the product obtained confirms that cellulose was successfully extracted from rice husk (Figure 4).

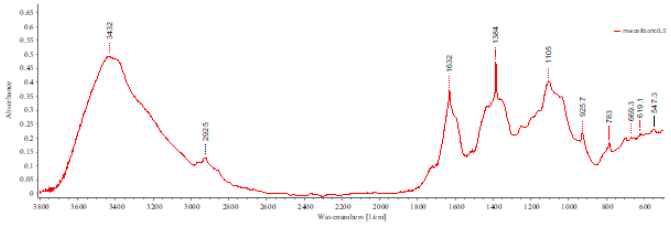

Figure 4 FT-IR spectrum of cellulose cross-linked with 0.5g of boric acid using a microwave.

Figure 5 and Figure 6 shows the FT-IR spectra of cellulose cross-linked with boric acid using microwave and refluxing methods. The peaks are almost similar, the new absorption bands 1438, 1251, 1193, 1032 and 925cm^{-1} was observed in both spectrums. However, they were not fully observed in figure 4, this is because the amount of boric acid during the synthesis was inadequate. The absorption bands at 3235 and 2927cm^{-1} present the functional groups of O-H and C-H stretching vibration. The absorption bands at 1438, 1251, 1193, 1032, 925 and 783 are attributed to the borate network as shown in Table 1. Borate network normally exhibited vibrational mode of infrared at three different regions, an absorption band between 800–1100cm^{-1} are characteristics of B-O stretching vibration of tetrahedral BO^{4-} units, 600–800cm^{-1} are due to bending vibration of borate segments and absorption band between 400–800cm^{-1} is associated with bending mode of B-O-B bridge in BO_3 and BO_4 units.[29,32] The reaction was conducted under reflux (80°C for 24hrs) and microwave irradiation, the products were comparable, by refluxing method, and anything beyond 1.0g of boric acid for 24hrs cannot be comparable with a microwave heating system as shown in figure 4. Therefore, microwave irradiation becomes more efficient than the conventional method.

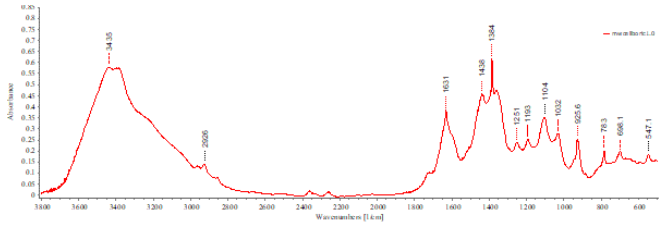

Figure 5 FT-IR spectrum of cellulose cross-linked with 1.0g of boric acid using a microwave.

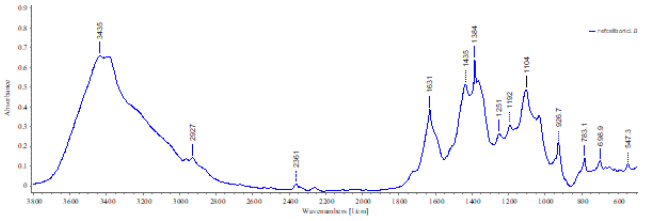

Figure 6 FT-IR spectrum of cellulose cross-linked with 1.0g of boric acid using reflux.

Table 1 Absorption bands and their assignments for FT-IR of SAH

Absorption bands (cm-1)	Assignment	Reference
685	B-O-B bending vibration	Rojas et al.,[29]
700	B-O-B bending vibration in borate ring	Ardelean and Toderas,[30]
850 – 1100	B-O stretching of tetrahedral BO4-	Kamitsos et al.,[31]
600 – 800	Bending vibration of various borate	Ardelean and Toderas,[30]
907	B-O stretching vibration of BO4- in tri, tetra, and pentaborate	Rojas et al.,[29]
1400	B-O stretching trigonal BO3 unit	Kamitsos et al.,[31]

X-ray diffraction of superabsorbent hydrogel

(Write a small preamble to introduce Figure 7 and Figure 8)

The extracted cellulose and cellulose cross-linked with boric acid were characterized by the X-ray diffraction (XRD) pattern. The diffractogram of cellulose and cellulose cross-linked with boric acid showed a pattern of a characteristic peak at 2θ=22° respectively. It is observed that the peak intensity of cellulose cross-linked with boric acid is higher than that of the cellulose, which indicated that the cellulose is not completely amorphous due to inadequate treatments with alkali material. A similar results was observed in our previous studies when crosslinking carboxymethylcellulose with 1, 2-ethanediol. The decrease in crystallinity plays a vital role in hydrogel degradability, water uptake and swelling ratio.[33] In a situation whereby the intensity of the hydrogel is lower than the cellulose, it indicates that there is a decrease in the crystallinity (material is more of amorphous).[34]

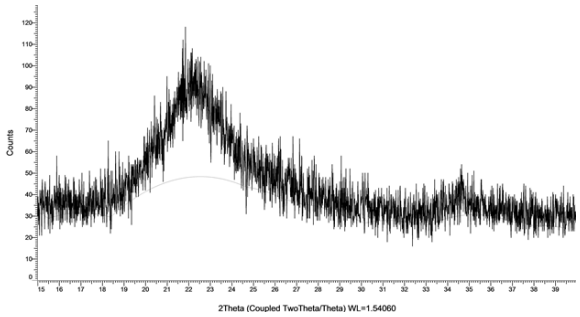

Figure 7 X-ray diffraction of extracted cellulose.

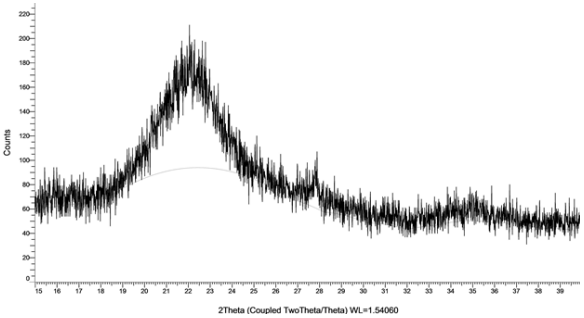

Figure 8 X-ray Diffraction of cellulose cross-linked with boric acid.

Optimizing synthesis conditions for super-absorbent hydrogels

Reaction time, microwave oven power out-put, and amount of crosslinker required were optimized by determining the percentage swelling of SAH prepared under varied conditions. Figure 9 shows the variation of percentage swelling with reaction time.

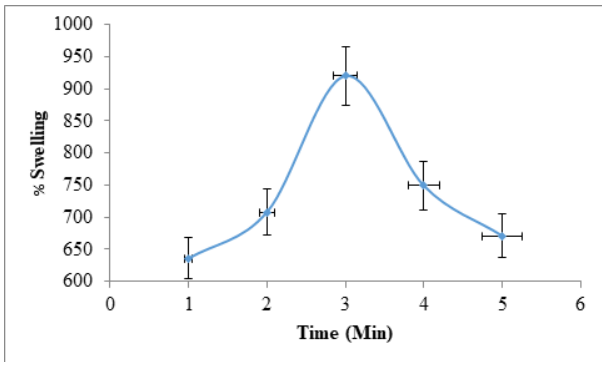

Figure 9 Variation of percentage swelling with reaction time (at power output of 6 equivalent 420 watts, 1.0 g of boric acid, 2 g of cellulose).

There is an increase in percentage swelling from 636–920% when the time was varied from 1–3 minutes as shown in Figure 9. As time increase from 3–5 minutes, the percentage swelling of superabsorbent decreases 920–671%. The increase in percentage swelling can be a result of the formation of hydrogen bonding between the functional groups on the superabsorbent hydrogel and water molecules. The bonding also delays the absorbed water of the hydrogel matrix and improves the retention capacity. Similar results were observed by[35] in the synthesis of rice husk ash (RHA) based superabsorbents hydrogel. The decrease in swelling capacity suggests that it has reached saturation and prolonging time while the power is maintained; therefore it reduces the diffusion rate.

The effect of varying the power output on percentage swelling using superabsorbent hydrogel is given in Figure 10. As shown, the percentage swelling increased from 648–915%, when the power output was increased from 2-6, this is equivalent to 140-420watts respectively. An increase in the power output from 6–10, which corresponds to 420–700 watts, was accompanied by a decrease in percentage of swelling. The highest percentage of swelling occurred at power output of 6 (420watts) and was recorded as optimum. As the power output increased, there was destruction between the hydrogen bonding existing in polymer, thus the percentage of swelling increased. Consequently, an increase in power output enhanced the swelling capacity. The decrease in the percentage of swelling might have been as a result of the inadequate entropy and internal energy, leading to the low rate of diffusion of water molecules into the hydrogel.

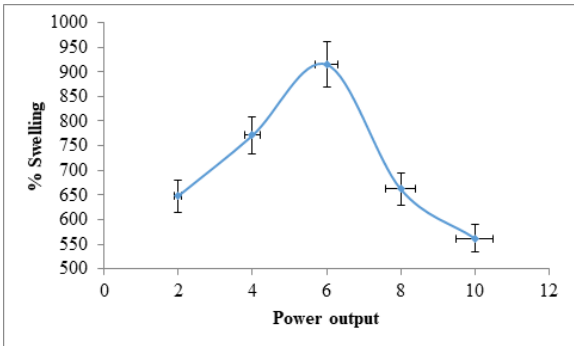

Figure 10 Variation of percentage swelling with power-output (at 3 minutes, 1.0 g of boric acid, 2 g of cellulose).

Figure 11 shows the effect of cross-linker on percentage of swelling. It is observed that the percentage swelling increased with an increase in the amount of cross-linker (Boric acid). The percentage

swelling increased from 646–986% when the amount of cross-linker (Boric acid) was increased from 0.5–1.0g. The graph indicated that a low amount of cross-linker led to less percentage swelling of the superabsorbent hydrogel, in comparison with a number of OH groups in cellulose, only a few were able to crosslinked, due to inadequate amount of boric acid , while other OH remains vacant. The extent of the formation of complex (crosslinking) will be small, due to the inadequate amount of boric is inadequate. The crystallinity is also reduced when there is less amount of the crosslinker.

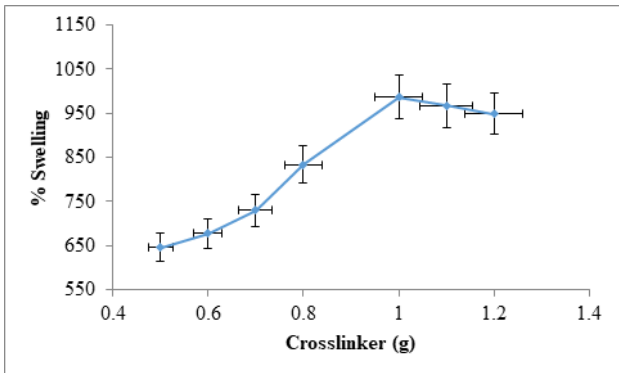

Figure 11 Variation of percentage swelling with amount of crosslinker (Boric acid) (at power out-put of 6 equivalent 420 watts, 3 minutes, 2 g of cellulose).

Conclusion

In this study, superabsorbents hydrogel was successfully synthesized from cellulose obtained rice husk crosslinked with boric acid using microwave irradiation and reflux method. By reacting the cellulose with boric acid, the crosslinked cellulose was confirmed and observed with Fourier transform infrared (FT-IR) and x-ray diffraction (XRD). The percentage of swelling of the hydrogel was achieved by varying the reaction time, power output, amount of boric acid and the amount of cellulose dose. Therefore boric acid is a very good crosslinking agent for cellulose, and microwave irradiation is more efficient than the reflux method. As part of the recommendation, this SAH can be applied in arid areas for agricultural practices towards addressing drought.

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None.

Conflicts of interest

The authors declared that there is no conflict of interest.

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