
SYNTHESIS AND CHARACTERIZATION OF SUPERABSORBENT HYDROGEL BASED ON SUGARCANE BAGASSE GRAFTED ONTO POLYACRYLIC

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ABSTRACT

Superabsorbents hydrogel were prepared by grafting of sugarcane bagasse on polyacrylic acid by using N, N'-methylene bisacrylamide as cross-linker and ammonium persulphate as initiator. Factors such as weight ratios of bagasse and acrylic acid monomer that affect the properties of the product were investigated. Properties of superabsorbent such as water uptake, gel fraction, morphological structure and thermal properties were also examined.

Keywords: Superabsorbent, Hydrogel, polyacrylic, Bagasse, gel fraction.

1-INTRODUCTION

Superabsorbent is hydrogel that has capacity to hold water within its pores, ranging from hundred to thousand times its weight. These network polymers form a class of materials that are potentially useful for variety of more specialized applications [1-5]. The water holding capacity of these hydrogels arises mainly due to presence of hydrophilic groups and their cross-linking structure [6-7]. Polysaccharides superabsorbents have greatly been paid attention in recent years, because of their biocompatibility, biodegradability, renewability and non-toxicity [8-9]. The most familiar method for the synthesis of these polymers is the free-radical graft polymerization of vinyl monomers onto polysaccharide backbones followed by cross-linking of their chains [10-11].

There are many researches on introducing of starch, Cellulose, Chitosan, Sodium alginate, lignin and Inorganic clays into the polymeric structure of superabsorbent in order to improve swelling property, reduce production cost and ensure biodegradability [12-15]. Few researches on superabsorbents based on plant waste as a source of cellulosic material have been appeared in recent years [16-17]. Sugarcane bagasse, one of the largest cellulosic agro-industrial wastes, is usually used in paper industry and as fuel. It is mainly composed of cellulose (about 50%), hemicellulose (about 25%) and lignin (about 25%), that are associated together by hydrogen and some other covalent bonds to form the network structure [18]. Cellulose is a homopolysaccharide while hemicelluloses are heteropolysac-

charides. Cellulose molecules have a strong tendency to form intra and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. Microfibrils build up fibrils and finally cellulose fibers. Hemicelluloses are amorphous and are associated and oriented along the cellulose while, lignin is amorphous and isotropic and incrusts both the hemicellulose and cellulose [19].

In our study, sugarcane bagasse grafted with acrylic acid was prepared and investigated as eco-friendly superabsorbent.

2- Experimental

2-1-Material

*Acrylic acid (AA) chemically pure grade, a product of Biochemica, Germany.

*The depithed bagasse was received from Masr-Edfu pulp mill at Aswan, Egypt.

*Ammonium persulphate (APS) analytical grade, a product of Sigma, Germany.

*N, N'-Methylene-bisacrylamide (MBA) chemically pure grade, a product of Shanghai chemical reagent, China.

*Potassium hydroxide (KOH), analytical grade, a product of Fluka chemie, Germany.

2- 2 Chemical analysis of bagasse sample

α -cellulose, ash and lignin contents of bagasse were determined according to Tappi standard T203, T211 and T 222, respectively. While

holocellulose content was determined according to Wise [20]. The values of chemical analysis were duplicated to ensure good results.

2-3 Preparation of bagasse-g-polyacrylic acid.

Appropriate amount of sugarcane bagasse was suspended in 20 ml distilled water into a three-necked flask equipped with stirrer, a reflux condenser, a nitrogen line and a thermometer. The solution was heated to 60 °C for 30 min and then purged with nitrogen for 15 min to remove the dissolved oxygen.

Mixture solution of 20 g AA (partially neutralized by 12.12 ml of 50% KOH solution), 0.1g cross-linker (MBA) and 0.1g initiator (APS) in 25 ml distilled water was added to the bagasse solution upon stirring. The water bath was kept at 70 °C for 3 h to complete polymerization. The gels formed were washed with distilled water and then dried to a constant weight at 70 °C. The products were ground and passed through 20-40 mesh sieves.

2-4 Determination of the gel fraction (GF)

A certain weight of bagasse-g-polyacrylic hydrogel samples were dried for 6h at 50 °C in an oven and were weighted (W_o). Then soaked in distilled water for 24h up to reach a constant weight and taken out from the swelling solution for removing the soluble part of the gels. The gels were dried again at 50 °C and weighted again (W_e). The gel fraction percent (GF %) was calculated from equation (1)

$$\text{Gel fraction (GF \%)} = W_e/W_o \times 100 \quad (1)$$

Where W_o and W_e are the weight of dried gel samples before and after soaking, respectively [21].

2-5-Water uptake (absorbency) measurement

A certain weight of bagasse-g-polyacrylic hydrogel samples were dried at 50 °C in an oven for 6h and were weighted (W_o).

The dried samples were soaked in distilled water, maintained for 12h and incubated at 37°C,

then weighted (W_s). The water uptake (absorbency) was determined using equation (2).

$$\text{Water uptake (absorbency) g/g} = (W_s - W_o) / W_o \times 100 \dots \dots \dots (2)$$

Where W_o and W_s are the weight of dry and swollen gel samples, respectively [22].

3- Results and discussion

3-1- Chemical constitution of bagasse.

The chemical analysis of bagasse is given in Table 1 in which the cellulose represents 54% of bagasse. Cellulose consists of β -D-glucopyranose residues linked together by β -(1-4) glycosidic bonds form long, linear chains. Each glucose residue contains three hydroxyl groups, which can be esterified or etherified to yield cellulose derivatives, consequently grafting forming hydrogel. In addition, the free hydroxyl groups have a strong affinity for polar solvents and solutes as swelling with water. During swelling, the hydrogen bonds between cellulose molecules are broken and replaced by hydrogen bonds between cellulose molecules and water[23].

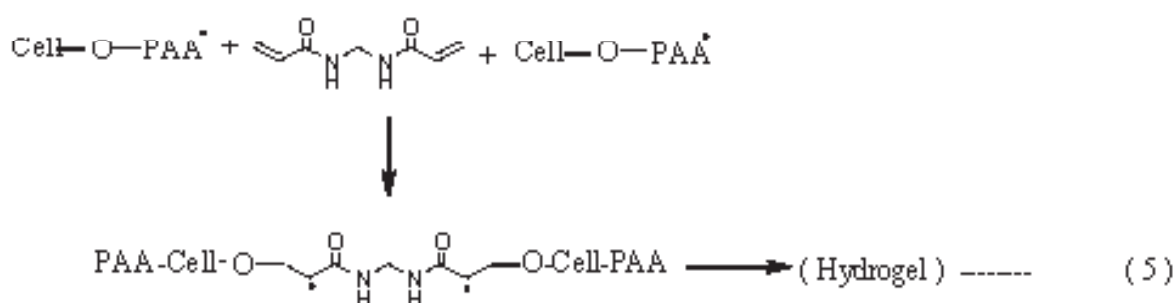
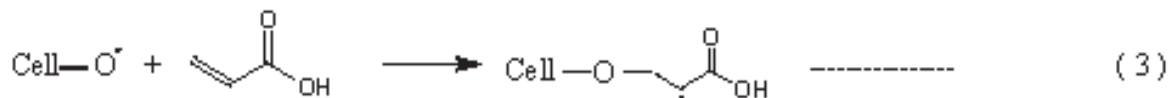
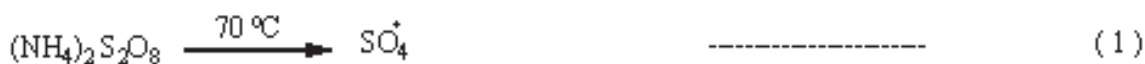
Table 1. Chemical analysis of bagasse.

Holocellulose %	α -cellulose %	Lignin %	Ash %
79.5	54	19.5	1.62

Bagasse consists of holocellulose (α -cellulose + hemicellulose), lignin and ash

3-2- Mechanism of bagasse-g-polyacrylic acid.

Bagasse-g-polyacrylic acid was synthesized via free radical mechanism in which the ammonium persulphate decomposes at the reaction temperature to give sulphate free radicals [24] (equation 1). These radicals attack one hydroxyl group of cellulose molecule generating cellulose free radicals (equation 2), which react with acrylic acid monomers, initiating graft copolymerization reactions of cellulose acrylic acid (equation 3). The propagation reaction continues forming cellulose polyacrylic acid radicals (equation 4). The free radicals attack N,N'-methylene bisacrylamide from both sides results in cross-linking of cellulose chains producing hydrogel network (equation 5).



3-3-Effect of bagasse content on gel fraction and water absorbency

Gel fraction and water absorbency data of the prepared superabsorbent samples incorporated with different amount of bagasse in distilled water are collected in Table 2 and graphically represented in Fig.1. It is clear that the amount of bagasse powder plays an important role in affecting the gel fraction percentage and water absorbency of bagasse-g-polyacrylic

superabsorbent. The water absorbency increases from 199 to 578 as the amount of bagasse increases from zero to 10 %. Further increasing of bagasse decreases the water absorbency. This may be attributed to the reaction between -COOH group in the polymer chain and -OH group in the polysaccharide chain of bagasse [25], enhancing the water absorbency until 10 % of bagasse. But if the gel contains more than 10 % bagasse then, it may fill the bagasse-g-

Table (2): Preparation of Bagasse-g-polyacrylic acid with different bagasse content.

Experimental no.	1	2	3	4	5	6
Weight of Bagasse (g)	0	0.5	1	1.5	2	2.5
Weight of Water (g)	0	20	20	20	20	20
Heating Temperature (°C)	0	60	60	60	60	60
Time (min.)	0	30	30	30	30	30
Weight of AA (g)	0	20	20	20	20	20
Add. Water (g)	0	15	15	15	15	15
Volume of 50% KOH (ml)	0	12.5	12.5	12.5	12.5	12.5
Weight of MBA (g)	0	0.1	0.1	0.1	0.1	0.1
Weight of APS (g)	0	0.1	0.1	0.1	0.1	0.1
Heating Temperature (°C)	0	70	70	70	70	70
Time of Reaction (h)	0	3	3	3	3	3
Water Absorbency (g/g)	199	282	412	578	210	-
Gel-fraction %	22	37	48	64	18	No gel

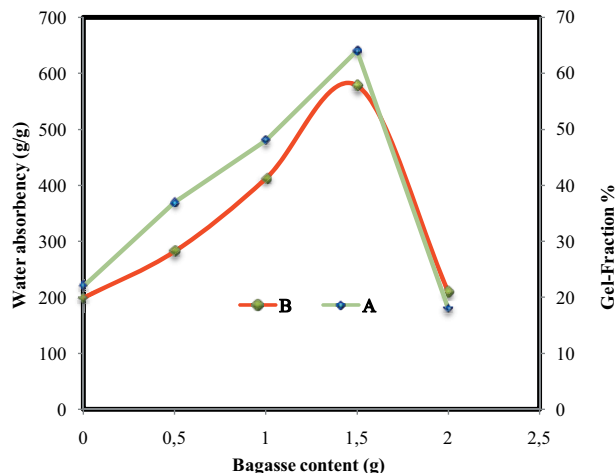


Fig.1 Effect of bagasse content on: (A) gel-fraction % and (B) water absorbency(g/g) .

polyacrylic network lowering the hydrophilic groups content and water absorbency.

The gel-fraction increases from 22 to 64 % as the amount of bagasse increases from zero to 10 %. If the percentage exceeds 10 then, the gel fraction will dramatically decrease; this may be due to a decrease in elasticity of the gel by increasing the crosslinking of the polymer.

3-4-FT-IR spectra analysis

The FT-IR spectra of bagasse, polyacrylic acid and bagasse grafted on polyacrylic superabsorbent were given in Fig. 2. Spectrum (a) represents the bagasse in which the strong band at

3411 cm^{-1} is the characteristic stretching vibration band of the O-H group and the appeared band at 2950 cm^{-1} corresponding to the stretching of C-H aliphatic. While the absorption bands at 1730 cm^{-1} and 1508 cm^{-1} are due to the stretching vibrations of carbonyl group and the peak at 1603 cm^{-1} represents the C=C aromatic ring of lignin. Moreover, the absorbance at 1421 cm^{-1} , 1325 cm^{-1} , 1263 cm^{-1} and 990 cm^{-1} corresponds to the skeleton vibration or aromatic ring breathing in lignin [26]. On the other hand, the peak at 1052 cm^{-1} represents the C=O stretching vibration in both cellulose and hemicelluloses. Cross-Liked polyacrylic (spectrum b) showed a bands at 3780 cm^{-1} and 3428 cm^{-1} which were attributed to the carboxylic group, band at 2924 cm^{-1} due to stretching and bending of CH_2 group and the band at 1630 cm^{-1} represents the C=O stretching vibration. While bagasse-g-polyacrylic superabsorbent (spectrum c) showed absorption bands at 1674 cm^{-1} and 1566 cm^{-1} corresponding to the stretching and asymmetric $-\text{COOH}$ group, respectively. The $-\text{COOH}$ stretching indicates the presence of PAA. The absorbencies at 1458 cm^{-1} and 1048 cm^{-1} represent the C=C and C=O stretching vibrations, respectively, which assure the formation of superabsorbent bagasse (i.e.) the product is a composite based on PAA and bagasse.

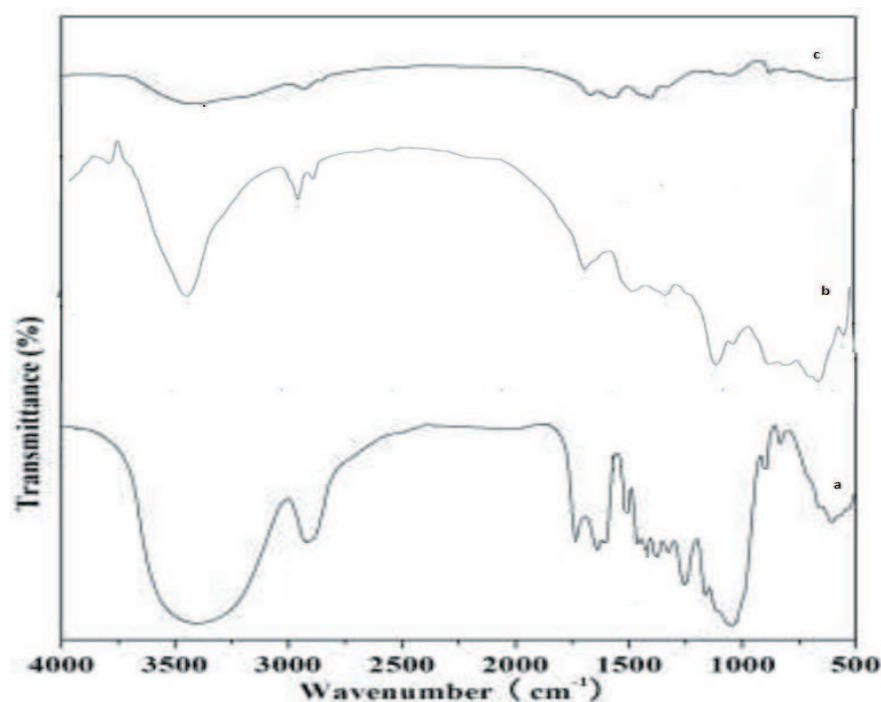


Fig. 2. FTIR spectra of Bagasse (a), PAA (b) and SB/PAA (c) superabsorbent containing 10 % Bagasse.

3-5- Morphology of bagasse-g-polyacrylic

SEM studies were carried out on a JEM- 5600

LV SEM instrument after coating the sample with gold film using an acceleration voltage of 20 K.V.

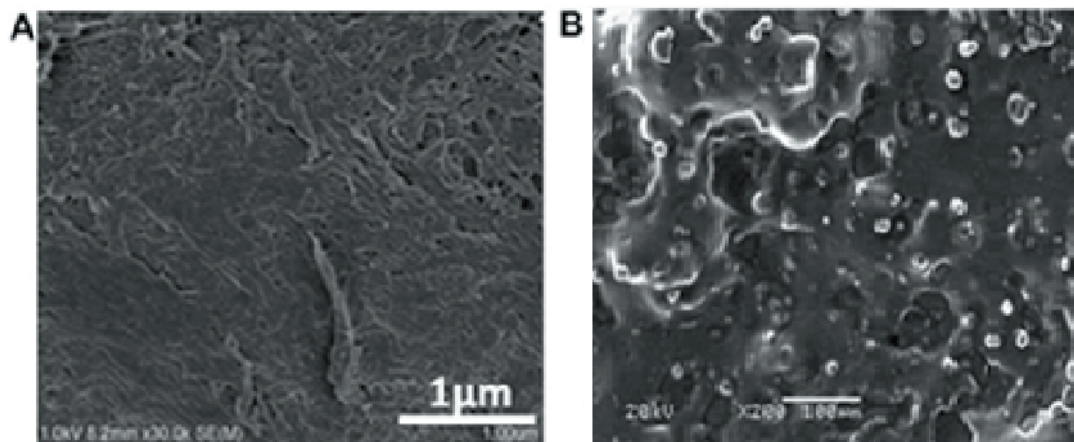


Fig. 3. ESM for dried (A) bagasse, (B) SB/PAA superabsorbent containing 10 % Bagasse

SEM pictures show the surface morphology of bagasse (A), and bagasse-g-acrylic composite (B) are depicted in Fig. 3. The smooth surface of bagasse (Fig. 3A) and the coarse surface structure of bagasse-g-polyacrylic (Fig. 3B) refer to the increase of water absorbency into the polymer network.

3-6- Thermal properties of bagasse-g-polyacrylic

TGA was recorded on a NietschestA – 449c Thermogravimetric analyzer, in the temperature range 25-600 °C at a heating rate of 10 °C / min.

TGA curves of cross-linked polyacrylic and bagasse-g-polyacrylic composite are shown in (Fig.4). The two samples showed the same loss at 50-200 °C indicating the loss of moisture. The

thermal decomposition of the cross-linked polyacrylic (Fig. 4A) was divided into two steps, the first one (at 230 °C up to 330 °C) corresponds to the decomposition of carboxylic group, and the second one (at 420 °C) corresponds to the decomposition of the PAA polymer chains. While the decomposition of bagasse-g-polyacrylic (Fig. 4B) was divided into three steps, the first one (at 220 °C) corresponds to the decomposition of bagasse and the second step (at 350 °C) was due to the decomposition of carboxyl groups. While the third one (at 430 °C) associated with the decomposition of the PAA polymer chains. However, the decomposition rate of bagasse-g-polyacrylic was lower than those for the decomposition of PAA polymer, confirming the higher thermal stability of superabsorbent than that of crosslinked-polyacrylic hydrogel.

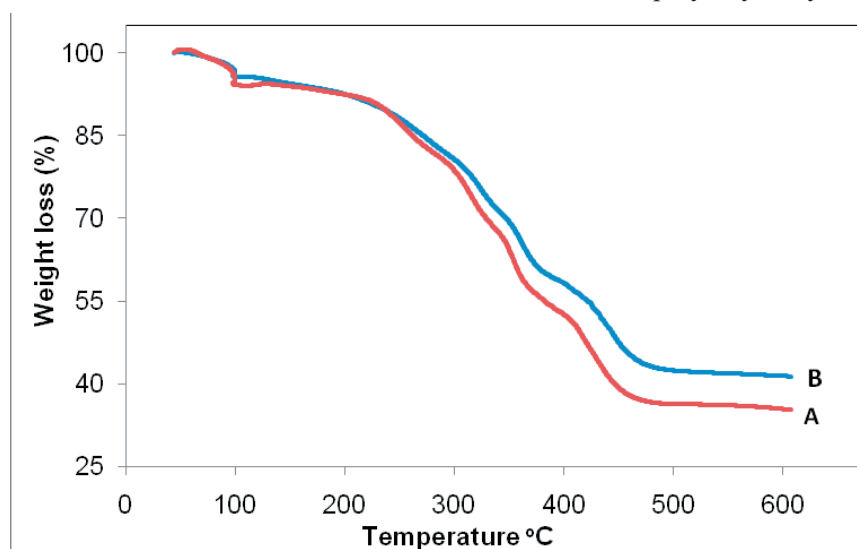


Fig. 4. TGA curves of PAA (A) and SB/PAA (B) superabsorbent at a heating rate of 10°C/min.

4-Conclusion

Bagasse-g-polyacrylic acid superabsorbent was synthesized by the graft co-polymerization reaction of bagasse and acrylic acid in aqueous solution. The highest water absorbency was obtained when the amount of bagasse was 10 % in our experimental condition.

Uses of bagasse as cellulosic and industrial waste in superabsorbent production significantly reduces the production cost and make it more environmental friendly.

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