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Screening of Superabsorbent Polymers in Barley Husk

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ABSTRACT

Superabsorbent Polymers (SAPs) as hydrogels are super-soaker organic materials - Carboxymethyl Cellulose (CMC) which swells in water to form a clear gel. These are different from conventional absorbent sponge in which water can be wrung out easily; the SAPs' hydrate gel particle retains the absorbed water even under pressure. This unique ability to hold absorbed water, even against pressure, is the primary benefit of using SAPs. Such SAPs have created a very attractive area in the viewpoint of super-swelling behaviour, chemistry, and designing the variety of final applications. Besides various applications, the most volume of SAPs world production (10^6 tons/year) is yet consumed in hygienic uses, i.e., disposable diapers (as baby or adult diapers, feminine napkins, etc.). Agro wastes like Barley husk can be a very potential resource to obtain CMC or SAPs. This paper discusses extraction of α -cellulose followed by carboxymethylation process to get CMC from barley husk. Absorbency tests of the CMC were performed by tea bag method and all the samples were characterized by FTIR.

KEYWORDS: Carboxymethyl Cellulose, barley husk, disposable diapers, Superabsorbent Polymers,

INTRODUCTION

Superabsorbent Polymers (SAPs) are high performance water absorbent and retention materials with three dimensional network structures. SAPs as hydro-gels, relative to their own mass, can absorb and retain extraordinary large amounts of water or aqueous solution (Buchholz, 1998). These materials can absorb water and other liquid up to thousand times of their own weight in relatively short time. They can also maintain the condition of swollen although under pressure (Ahmadpour, 2007). SAPs materials function by the mechanism which may be anticipated by combination of mechanisms of physical entrapment of water via capillary forces in their macro-porous structure (e.g., soft polyurethane sponge), hydration of functional groups (e.g., tissue paper) and essentially dissolution and thermodynamically favoured expansion of the macromolecular chains limited by cross-linkages.

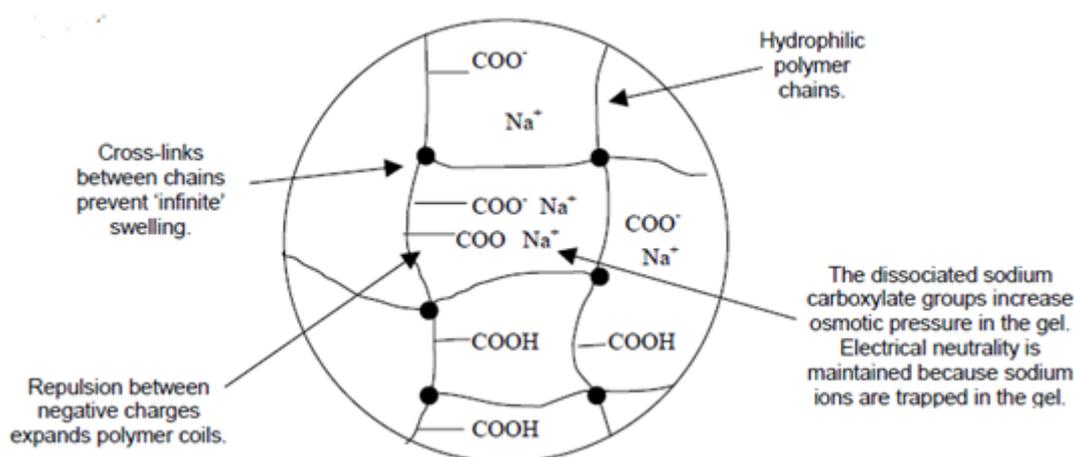


Fig. 1. Diagrammatic representation of part of the polymer network (Buchholz,1997).

Note: The polymer backbone in SAP is hydrophilic i.e. ‘water loving’ because it contains water loving carboxylic acid groups (–COOH). When water is added to SAP there is a polymer/solvent interaction; hydration and the formation of hydrogen bonds are two of these interactions.

This unique ability to hold absorbed water, even against pressure (Cooke, 2002), is the primary benefit of using superabsorbent polymers. These ultrahigh absorbing materials can imbibe de-ionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g) (Omidian, 2004).

Table 1.

Water absorbency of some common absorbent materials in comparison with a typical commercial SAP sample (Buchholz, 1998).

Absorbent Material	Water Absorbency (Wt %)
Superab A-200 ^a	20200
Cotton ball	1890
Wood pulp fluff	1200
Soft polyurethane sponge	1050
Facial tissue paper	400
Whatman No.3 filter paper	180

^aAgricultural SAP produced by Rahab Resin Co., Ltd., Iran (2007) [www.rahabresin.com] Zohuriaan-Mehr M.J. (2006)

Water absorbing polymers, classified as hydrogels, when cross-linked absorb aqueous solution through hydrogen bonding with water molecule (Kabiri, 2003). Their ability to absorb water is a factor of the ionic concentration of the aqueous solution. In de-ionized and distilled water, a SAP may absorb 300 times its weight (from 30 to 60 times its own volume) and can become up to 99.9% liquid, but when put into a 0.9% saline solution, the absorbency may drop to 50 times its weight (Kelco, 2015). The presence of valence cations in the solution impedes the polymer's ability to bond with the

water molecule (Brannon, 1990). The total absorbency and swelling capacity are controlled by the type and degree of cross-linkers used to make the gel. Low-density cross-linked SAPs generally have a higher absorbent capacity and swell to a larger degree. These types of SAPs also have a softer and stickier gel formation (Heinze, 2001). High cross-link density polymers exhibit lower absorbent capacity and swell, but the gel strength is firmer and can maintain particle shape even under modest pressure. This makes them ideal for use in water absorbing applications such as baby nappies and adults incontinence pads to absorbent medical dressings and controlled release medium.

Besides various applications, the most volume of SAP world production (10^6 tons/year) is yet consumed in hygienic uses, i.e., disposable diapers (as baby or adult diapers, feminine napkins, etc.). Evidently, SAPs have created a very attractive area in the viewpoint of super-swelling behaviour, chemistry, and designing the variety of final applications (Pairote, 2017). For example, the majority of women in rural areas use reusable cloths to absorb menstrual blood (Langer, 2015). Lack of awareness about menstrual hygiene marked by limited resources for cleanliness has a severe impact on the school attendance of female students in the rural areas of Nepal. The awareness of practices and access to facilities needed to maintain good hygiene during menstruation are generally found to be lacking (Water-Aid, 2010). This paper discusses the screening of SAPs to be used for sanitary towels from local agro-wastes of Barley husk (Lysac Technologies, 2008) as it contains no lignin, and pectin (Table 2, Pitaloka, 2013).

Table 2.

Chemical Composition of Several Types of Fibers (%-w) (Pitaloka, 2013)

Fibre	Cellulose	Hemicellulose	Lignin	Pectin	Fat/Wax
Cotton	90-99	-	-	-	-
Hemp	67-78	16-18	35-55	0.8	0.7
Jute	51-78	12-13	10.0-15.0	2-44	05
Sisal	50-74	10-14	8-11	01	02
Water hyacinth	60	08	17	-	-
Barley	48	-	-	-	-
Oat	44-53	-	-	-	-
Rice straw	38.3	38.3	31.6	11.8	
Rye	50-54	-	-	-	-
Wheat straw	39	38.7	17	-	19
Sugarcane Bagasse	43.6	33.5	18.1	-	0.8

EXPERIMENTAL METHOD

The raw material barley husk was well dried in sunlight and ground using grinding machine into 52, and 100 mesh (Brass Sieves, Endecotts Ltd., London, England, 2016). The powder (mesh 52 & 100) samples were subjected for extraction.

- *Extraction:* Finely ground sample of barley husk powder was treated with 2:1 ratio by volume of toluene and ethanol mixture in a conical flask. The conical flask with this mixture was placed in a water bath maintained at 85°C for 3 hrs, followed by filtration to obtain the extract of the barley husk.
- *1st Bleaching:* 6% sodium hypochlorite (NaClO) + extract in conical flask; the mixture of the flask was then placed in the water bath at 80°C for 1hr.

- *1st hydrolysis with NaOH:* Sodium hydroxide (NaOH) of various concentrations (table-3) was prepared; 100 ml of NaOH was mixed with 1st bleached samples in conical flasks. The flask was placed in water bath maintained at 60°C. After the hydrolysis, the materials were filtered and washed until sodium hydroxide was completely washed off (checked with phenolphthalein).

Table 3.

First hydrolysis with NaOH

Samples	Concentration of NaOH	Teperature (°C)
B52 α_1	0.1	60°C
B52 α_2	0.4	
B52 α_3	0.8	
B52 α_4	1.5	
B100 α_1	0.1	
B100 α_2	0.4	
B100 α_3	0.8	
B100 α_4	1.5	

- *2nd bleaching with 1% NaClO:* 1% sodium hypochlorite (NaClO) was prepared and 100 ml of 1% sodium hypochlorite was poured into the sample (already hydrolysed with NaOH) in a 500 ml conical flask. The mixture of the flask was then placed in a water bath at 75°C for 3 hrs. Then the samples were subjected for second hydrolysis with 5% HCl.
- *2nd hydrolysis with 5% HCl:* 5% of hydrochloric acid (HCl) was prepared; 100 ml of the acid was mixed with the bleached sample in conical flask. The flask was placed in the water bath maintained at 65°C for 6 hrs. The materials were then filtered and washed until HCl was completely washed off (checked with methyl orange indicator).



Fig.2. A Sample (B100 α_4) after 2nd bleaching

- *Carboxymethylation:* The fine dry samples (after 2nd hydrolysis) were treated with the mixture of ethanol and iso-propanol (1:7 ratios) then 15 ml of 1M NaOH was poured into the mixture. Continuous stirring was performed using vibrator at 400 osc/min; 15 ml of glacial acetic acid was added with continuous stirring. The reaction temperature and the reaction time were controlled. The mixture was filtered off and suspended in 200 ml of methanol overnight. The mixture of methanol and sample was filtered, washed with 70% ethanol 4 times and the residue was allowed to dry in oven at 60°C.

- **Absorbency Test:** Tea bag method was used in this research for absorbency testing of the research samples. The SAP sample was placed into a tea-bag (acrylic/polyester gauze with fine meshes) and the bag was dipped in an excess amount of water (saline could be used) for one hour to reach the equilibrium swelling. Then excess water/solution was removed by hanging the bag until no liquid dropped off. The tea bag was weighed (W_1) and the *swelling capacity* (S_c) was calculated by using eqⁿ (1). The method's precision has been determined to be around $\pm 3.5\%$.

$$S_c = (W_1 - W_0) / W_0 \dots\dots\dots (1)$$

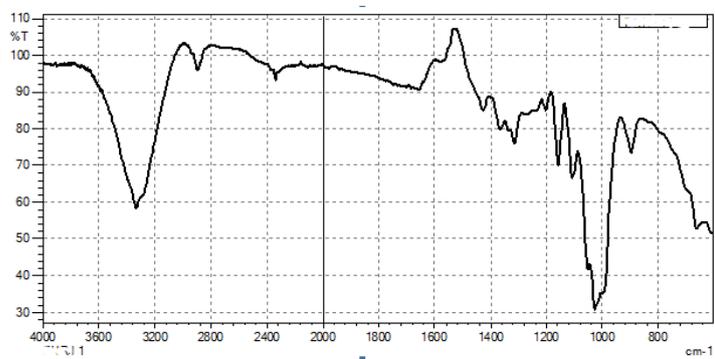
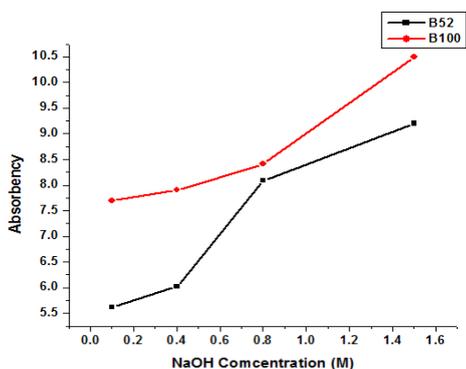
RESULTS AND DISCUSSION

The absorbency data of the barley husk samples both 52 and 100 mesh showed increasing pattern with both the NaOH concentration and sample particle mesh (size); B_{100} mesh (B stands for Barley) showed comparatively higher absorbency [Fig 3(a)].

Table 4.

Comparative study of Absorbency of B_{52} and B_{100} meshes of Barley husk

Samples	NaOH Concentration	Absorbency of B_{52} Mesh	Absorbency of B_{100} Mesh
α_1	0.1M	5.62	7.7
α_2	0.4 M	6.02	7.9
α_3	0.8M	8.09	8.41
α_4	1.5M	9.20	10.50



(a)

(b)

Fig. 3 (a) Variation of Absorbency with NaOH concentration and mesh type (B_{100} & B_{52} Mesh)
 (b) FTIR of $B_{100}\alpha_4$ sample

The FTIR of B₁₀₀ α₄ (Fig. 3b) and all the other samples showed the peaks corresponding to the backbone of the cellulose molecule at 3435 cm⁻¹ (broad absorption band due to stretching of –OH groups and intermolecular and intra-molecular hydrogen bonds), 2916 cm⁻¹ (C–H stretching), 1422 cm⁻¹ (–CH₂ scissoring), 1327 cm⁻¹ (–OH bending) and 1061 cm⁻¹ (CH–O–CH₂ stretching). The peak at 1601 cm⁻¹ corresponds to COO⁻ in the FTIR spectrum of B₁₀₀. Thus, the FTIR spectrum of B₁₀₀α₄ indicates the presence of carboxymethyl cellulose (CMC) in barley husk.

LIMITATIONS

This research was confined to only one agro waste, barley husk, varying only few parameters.

CONCLUSION

Barley husk is found to be a potential agro-waste for the mass scale production of SAPs. Its absorbency is greatly affected by particle size of the sample, and concentration of hydrolyzing solution like NaOH.

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