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One Pot Synthesis of Green Detergents from Biowastes

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ABSTRACT

Biowastes like barley husk, corn cob, sugarcane bagasse etc. are rich in hemicelluloses and can serve as cheap raw materials to develop eco-friendly, non-ionic and biodegradable C_5 surfactants. In this paper, we used these hemicelluloses as a raw material for the synthesis of xylose based surfactants using mild conditions in a one-step method. The synthesized detergent was identified by Co-TLC and spectral data comparison with standard *n*-decyl xyloside. It was then checked for several parameters (like solubility, wettability, surface tension, emulsion stability, cleaning action, foaming ability, cytotoxic activity and biodegradability). The detergent is found to have low bio-toxicity, is eco-friendly and shows good surfactant properties like low surface tension, high wettability, good foaming properties with rapid collapse and high solubility. The results confirmed that the one-step synthetic methodology used in this research paper for the preparation of environment friendly surfactant is potentially economical and eco-friendly.

Keywords- biodegradable, cytotoxic activity, D-glucose, D-xylose, eco-friendly, L-arabinose and environmentally friendly.

INTRODUCTION

Hemicelluloses, the polyoses have currently been shown to be a promising alternative to fossil compounds (1-2). As hemicelluloses cannot be digested by human beings, so they do not put any burden on food supplies. The bio-wastes such as barley husk, corn cob, and sugarcane bagasse are rich in hemicelluloses. Continuous efforts are being, to improvise integrated lignocellulosic bio-refineries for best use of the crop-sourced resources, for example, the detergent industries are looking for some green, sugar-based surfactants for the last few decades. Detergents have been developed based on glucose such as that obtained from starch (3-6). Alternatively, a pentose-base was used for surfactants obtained from agricultural wastes (7-11). Thereby providing interest in the surfactant market, as these surfactants possess high detergent properties with a better environmental profile. In continuation of our research work (12), we have chosen biowastes (barley husk, corn cob and sugarcane bagasse) for the synthesis of green detergent (Figure-I). The process follows the acid pre-treatment of raw materials followed by the addition of *n*-decyl alcohol. As a result, hemicellulose is converted into decyl glycosides (bio-degradable C-5 surfactants

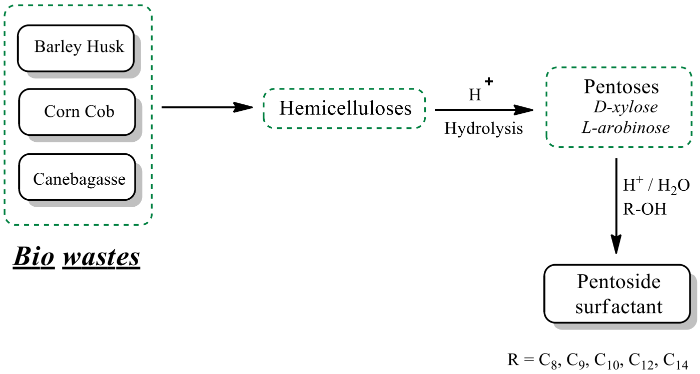
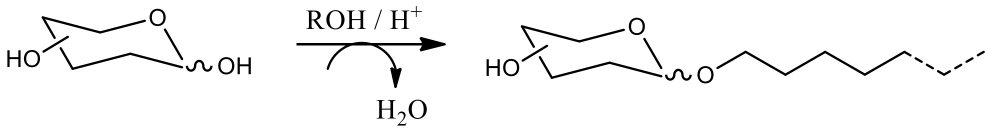


Figure-I. General scheme for the synthesis of pentoside surfactant from biowastes

MATERIALS AND METHODS

Infrared (FTIR) spectra were obtained from a Spectrophotometer instrument (Perkin Elmer-2000). ^{1}H NMR spectra taken from a Bruker Avance (400 MHz) and ^{13}C NMR spectra were recorded on Bruker Advance (100 MHz) using tetramethylsilane (TMS) as an internal standard and $CDCl_3$ as solvent. TOF ES+ Mass spectra (m/z) were obtained from Micromass Autospec LCTKC455. Elemental (CHNS/O) analyses were recorded on a Perkin Elmer series 11, CHNS/O analyzer 2400. Biowastes (barley husk, corn cob and sugarcane bagasse) were used after being chopped with a mixer in order to obtain fine powder.

Procedure for synthesis of sugar based detergent (*Scheme 1*): 2 g of powdered biowaste (barley husk/ corn cob/ sugarcane bagasse), 8 g of *n*-decanol, 0.21 mL sulfuric acid and 1 mL distilled water were taken in a round bottom flask and progressively heated to 100 ^{0}C in an oil bath for two hours with vigorous stirring. The reaction mixture was filtered and the reaction content was neutralized with NaOH solution. The yellow coloured solid that was obtained, was filtered and washed repeatedly with acetone. The solid was dried and its detergent characteristics (12) were determined and compared with those of commercially available detergents.



Scheme 1: Synthesis of sugar based detergent from sugarcane bagasse hemicellulose under acidic condition

***n*-Decyl xylosides**

IR: ν_{max} (film)/cm^{-1}: 3378 (O-H), 2919, 2852 (C-H), 1469, 1377, 1245, 1144, 1114, 1044; ^{1}H NMR (□, $CDCl_3$, 400 MHz): 4.04 (d, 1H, □-D-pyranoside, J = 7.2 Hz); 4.76 (d, 2H, □-D-pyranoside, J = 4.7 Hz); 4.88 (s, 1H, □-D-furanoside); 4.96 (d, 1H, □-D-furanoside, J = 4.4 Hz) (Figure-II); ^{13}C NMR (□, $CDCl_3$, 100 MHz): (□-D-pyranoside); 98.96 (□-D-furanoside) (Figure-III); 103.67 (□-D-pyranoside) ; *m/z* calculated for [$C_{15}H_{30}O_5 + Na^+$], 313,1991, found 313,1980; Elemental analysis ($C_{15}H_{30}O_5$): Calculated C = 62, 04 %; H = 10.41 %. Found C = 60.02 %; H = 10.55 %.

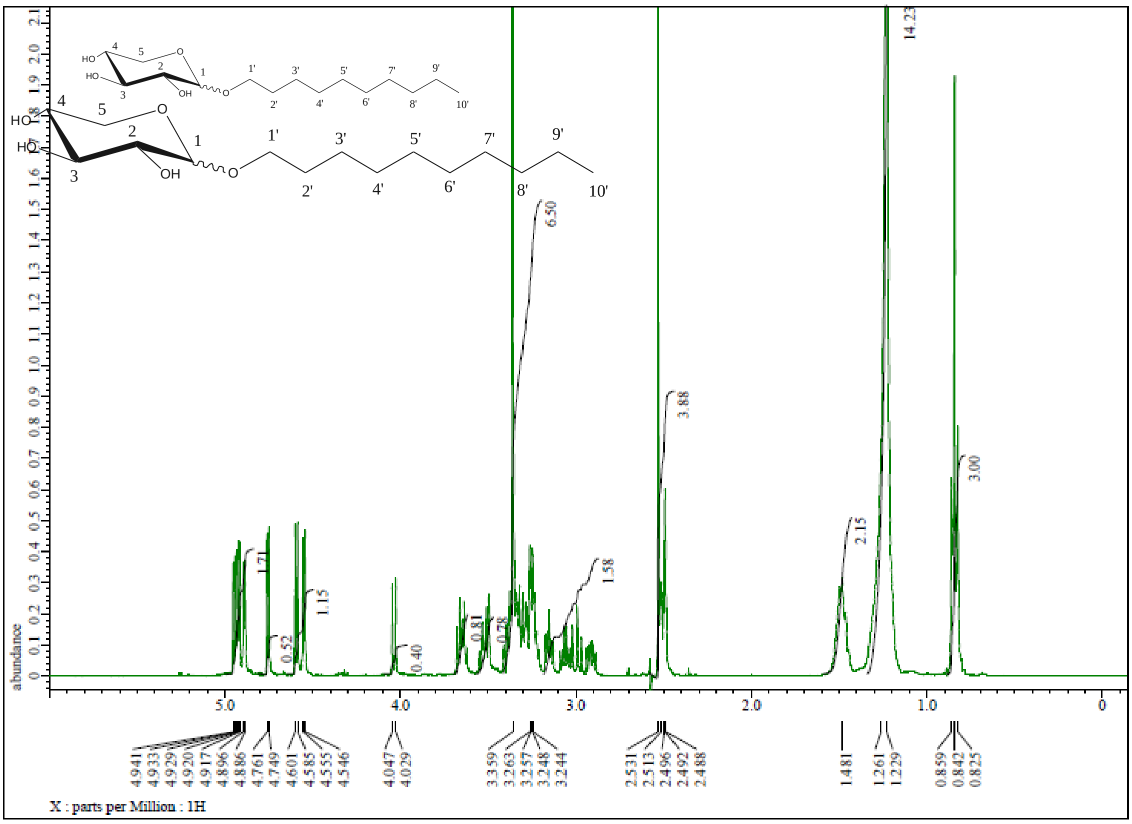


Figure-II. ^{1}H NMR spectra for the *n*-decyl xylosides

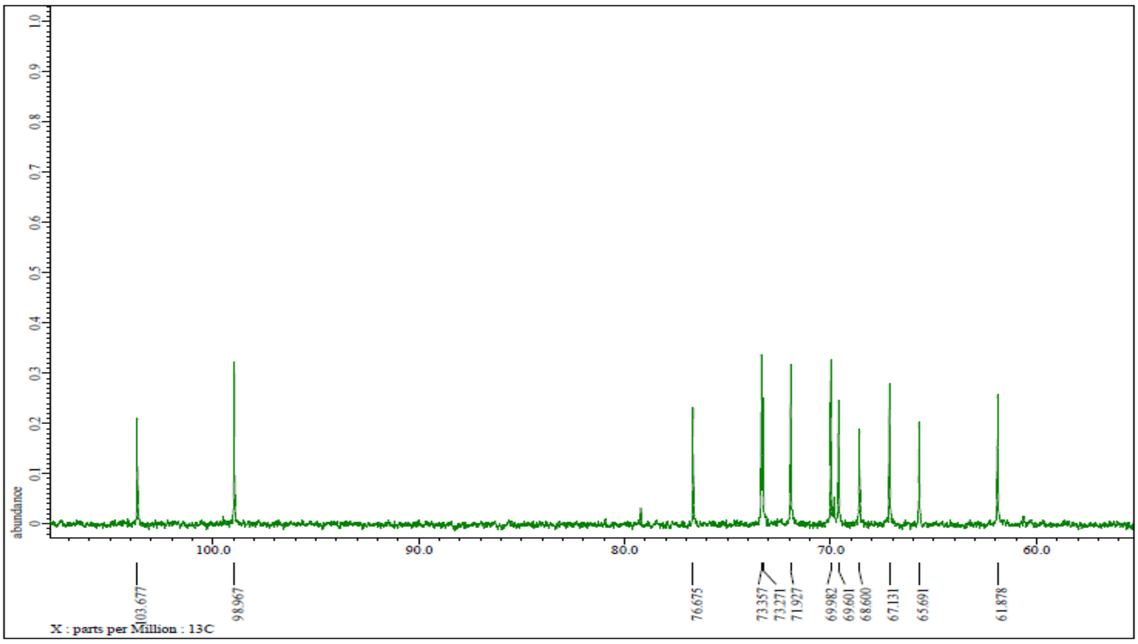


Figure-III. ^{13}C NMR spectra for the *n*-decyl xylosides

Study Of Different Properties Of Synthesized Detergents

pH: 0.2% solution of synthesized surfactant was prepared and pH was determined using the calibrated pH meter.

Surface tension: Surface tension was calculated for 0.2% solution of synthesized detergent using Stalagmometer apparatus by following the drop weigh method (13).

Foaming ability test: 8 mL of 0.2% detergent solution was taken in a labelled test tube and shaken 10-20 times. The time was reported for disappearance of 2 mm foam in a test tube (14).

Wetting performance test: 0.8 g cotton threads were kept on the top of the 100 mL of 0.5 % synthesized detergent solution. Time was recorded for the threads to sink to bottom of the beaker.

Emulsion stability test: 1 mL oil (i.e. mustard oil) was added to 15 mL of 1 % solution of prepared detergent and vortexed for 2 minutes. Time was recorded till detergent solution became clear.

Hard water test: 25mL of 1% synthesized detergent solution was added in three labeled test tubes. Then 2 mL of 5% magnesium chloride, 5% calcium chloride and 5% ferric chloride was added respectively to the three test tubes. Conclusion was drawn based on the precipitate formed.

Biodegradability test: BOD5 test carried out with 100 mg/L of synthetic detergents (15, 16) in dark for 5 days at 20 ^{o}C. 5ml of inoculum of water from the drain was added as microbial source. Diluents buffer with inoculum without the detergent sample was taken as a control. The oxygen consumed initially and after 5 days was measured using oxygen meter.

Hemolytic activity (Cytotoxic Test): 20 µL RBC solution and 980 µL PBS were taken in an eppendorf and marked as a control tube (17). In the reference eppendorf (100% lysis), 980 µL of triton X-100 (1%) and 20 µL of RBC were added. For the test 100 µL of the synthesized detergent solution, 880 µL of PBS and 20 µL of RBC were added. All eppendorfs were incubated for 10 minutes at 37 ^{o}C and centrifuged. Absorbance were recorded at 540 nm.

Cleaning action: Four types of stains (mud, ketchup, tea and coffee) were applied on the cotton cloth and the cloth dried for 24 hrs. The cloth was soaked for 15 minutes in 250 mL of 0.2% synthesized detergent solution and the stained cloth was stirred in detergent solution for 20 minutes. Finally the cloth was washed with running water and dried at room temperature (12).

RESULT AND DISCUSSION

In the present work, we have succeeded to standardize the procedure for conversion of barley husk, sugarcane bagasse and corn cob hemicelluloses into alkyl pentoside surfactants in a "*single step in one pot*".

The concentration of acid and water as well as the temperature of the reaction was varied with the aim of converting the highest amount of hemicelluloses into alkyl pentosides. Using 20% conc. H_2SO_4 and 50% H_2O w.r.t the weight of the bio-waste powder gave the maximum yield. The detergent prepared from barley husk was further purified using adsorption column chromatography. The purified xyloside was characterized by co-TLC comparison with standard n-decyl xyloside (Figure-IV) and based on its spectral studies such as IR, ^{1}H NMR & ^{13}C NMR.

Analysis of the Synthesized Decyl xyloside (surfactant)

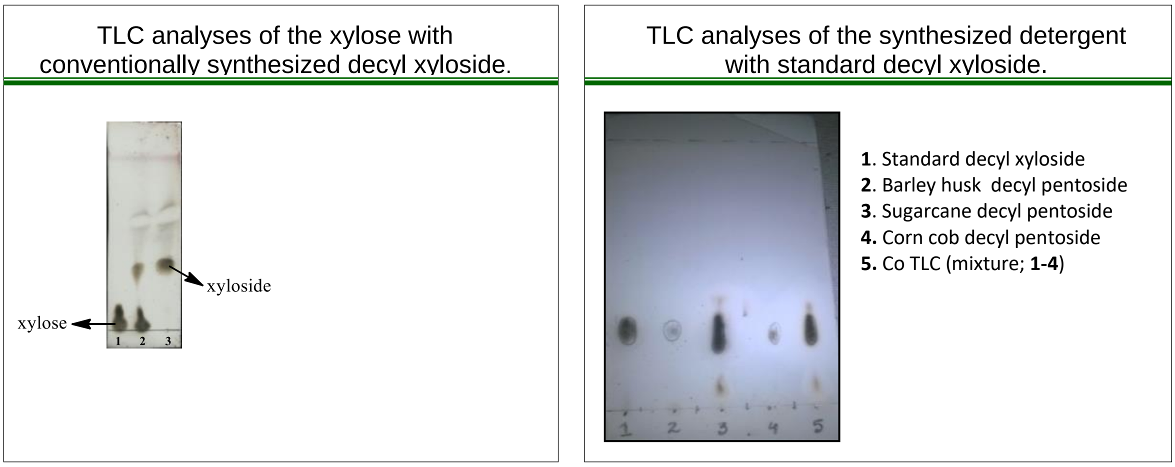


Figure-IV. Study of TLC behavior of the synthesized detergent.

<u>Cleaning Action of Synthesized Detergent (</u><u>Figure-V</u>**<u>):</u>**

Washing in water only (as control):

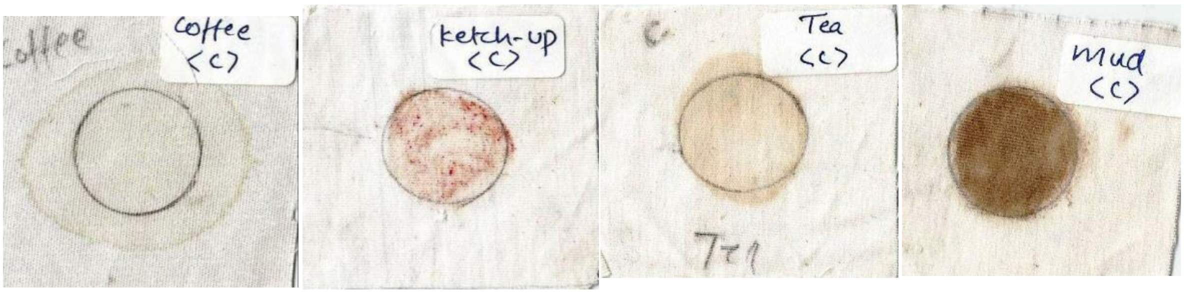


Figure-V. Cleaning action of synthesized detergent (as control)

Washing with 0.2% synthesized detergent solution (Figure-VI)

Figure-VI. Cleaning action of synthesized detergent on coffee, ketch-up, tea and mud stains.

The resulting alkyl pentoside from barley husk was tested[12] for its surfactant properties and the observations are listed in Table-I

Table I: Study of synthesized bio detergent.

S. No.	Parameters Studied#	Observations
	Solubility in cold water	100%
	pH	7.88
	Surface tension (dyne/cm)	26.80
	Foaming stability (Foam disappeared)	Good foam with collapse Time of 5 min.
	Wettability	High
	Emulsion stability	> 1 hr
	Hard water test	no scum formation
	Biodegradability	>60%
	Cytotoxic test	35 %

 # All studies were performed at room temperature using water as control.

CONCLUSIONS

In view of the growing importance of valorization of biowaste, we for the first time report the synthesis of sugar-based detergent from biowaste like sugar cane bagasse, corn cob and barley husk. The extraction and synthesis of detergent from biowaste is done using Green chemistry protocols. It uses a single step hemicellulose extraction and surfactant synthesis procedure at atmospheric pressure and low temperature, thereby reducing equipment and energy costs. This, developed and standard process, does not require a multi step (several processes) glycosylation process. We have developed an optimized method to explore the best use of pentose-based detergents
(surfactants) in the various laundry industries. The development process fits with the green chemistry approach as the extraction and synthesis of detergent from bio-waste is done using a single step, at lower temperature and atmospheric pressure, thereby reducing equipment and energy costs. The detergent is eco-friendly, has low bio-toxicity and shows good surfactant properties like low surface tension, high wettability, good foaming properties with rapid collapse and high solubility. It is economically viable with no negative impact on food supply. The detergent can serve as an alternative to petroleum-derived hydrocarbons based detergents.

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