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Studies on effects of different processing methods on nutritional qualities of hydrolyzed starch-resistant from rice industry By-product (Paddy straw)

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Abstract

Present investigation had been formulated to study the effects of different processing methods on nutritional, phytochemical improvement of non digestible class of carbohydrate i.e. cellulose and hemicelluloses. It is also called as starch resistant. The goal of hydrolysis of starch is meant for disintegrating resistant starch to hydrolyzed form and utilization of hydrolyzed carbohydrate to different value added food products. Various pretreatment techniques change the physical and chemical structure of the lignocellulosic biomass and improve hydrolysis rates. During the past few years a large number of pretreatment methods have been developed, including alkali treatment, acid treatment and others. Many methods have been shown to result in high sugar yields, above 90% of the theoretical yield for lignocellulosic biomasses such as woods, grasses, corn, and so on. The overall aim of this study was to improve the potential of economically using lignocellulosic biomasses by developing efficient pretreatment process and by optimizing the operating parameters of these novel processes. This research explored multiple biomass treatments (acid treatment, alkali treatment, pre-soaking followed by alkali treatment).

Keywords: Lignocellulosic biomass, acid treatment, alkali treatment

Introduction

Lignocelluloses are the structural polysaccharides of plants that composed of cellulose (~50%), hemicellulose (~30%), and lignin (~20%), and are widely distributed among the vascular plants. Cellulose and hemicellulose are polysaccharides composed of simple sugars; whereas, lignin is a complex network of aromatic alcohols. In general, hemicelluloses and lignin provide an amorphous matrix to which crystalline cellulose micro fibrils are dispersed (Cellulose micro fibrils are stabilised by intra- and inter-molecular hydrogen bonds, and are surrounded by hemicellulosic polymers. The cellulose-hemicellulose matrices are protected by lignin, an amorphous insoluble polymer which impedes the microbial attack on internal cellulosic structures (Bluefire ethanol 2010) [2].

Lignocellulosic biomass is principally composed of cellulose, hemicellulose and lignin. The cell wall of lignocellulosic biomass is a composite material of crystalline cellulose fibrils bound by non-crystalline hemicellulose and surrounded by a matrix of hemicellulose and lignin. The composition of biomass is different depending on the species and environmental conditions (Chen *et al.* 2007) [4]. The compositions of biomass and interaction of these components in the cell wall affect the hydrolysis of carbohydrates; therefore, understanding each component is important to efficiently utilize lignocellulosic biomass. Lignocellulose is the most abundant renewable biomass with a worldwide annual production of 1×10^{10} MT. Lignocellulose, the most abundant renewable biomass on earth, is composed mainly of cellulose, hemicellulose and lignin. Both the cellulose and hemicellulose fractions are polymers of sugars and thereby a potential source of fermentable sugars. Lignin can be used for the production of chemicals, combined heat and power or other purposes. Research is focussed on converting biomass into its constituents in a market competitive and environmentally sustainable way (Sanchez and Cardona, 2007) [3].

Lignocellulosic biomass is attractive feedstock because of affordable price and high polysaccharide content; however, it is not easy to use lignocellulosic resources for ethanol and other chemicals production.

In particular, several factors including lignin, hemicellulose, crystallinity of cellulose, lignin-carbohydrate complex, degree of polymerization, ash content, pore size and surface area are the native recalcitrance of lignocellulosic biomass to hinder biological conversion. The native form of lignocellulosic biomass can be partially digestible by enzymatic hydrolysis for this reason retreatment is necessary to overcome the recalcitrance and convert biomass more efficiently (Mussatto *et al.*, 2004)^[5]

Pretreatment involves the alteration of biomass so that (enzymatic) hydrolysis of cellulose and hemicellulose can be achieved more rapidly and with greater yields. Possible goals include the removal of lignin and disruption of the crystalline structure of cellulose. The following criteria lead to an improvement in (enzymatic) hydrolysis of lignocellulosic material: Increasing of the surface area and porosity, Modification of lignin structure, Removal of lignin, (Partial) depolymerization of hemicellulose, Removal of hemicellulose, reducing the crystallinity of cellulose.

Various pretreatment methods have been developed to change the physical and chemical structures and break down the hemicellulose and lignin shield efficiently. However, pretreatment is still one of the most expensive stages within lignocellulosic biomass conversion process. Developing effective pretreatment methods and finding optimal operating conditions can contribute to overcoming the cost barriers of biomass utilization. Minimizing energy, chemical and water inputs, preserving cellulose and hemicellulose fractions, avoiding size reduction and limiting formation of inhibitors are key issues to develop cost-effective pretreatment methods (Sarkar *et al.* 2008)^[7]

Material and methods

Raw material:

The rice straw (obtained from *Oryza sativa L.* "harvested in early July) was acquired from local producers). The fresh raw material was dried at 45 °C for 48 hours in an oven (Bio-Technics, India).

Methodology

Mechanical comminution

The chipping of rice straw was done by hand only using chopper/knife. The rice straw was subjected to drying in hot air oven at 50 °C for 48 hr. Two step grinding procedure was followed to obtain particles of desired size. Multipurpose ball mill was used for chipping and immediately after that the biomass is grinded through small size hammer mill. The dried and chopped rice straw was fed through the hopper in multipurpose ball mill. The size reduction was done by impact and attrition. A tray was placed exact below the exit channel and the grinded biomass (rice straw) is collected. Mainly to obtain coarse size the biomass was subjected to small size hammer mill, due to impact force the particle size was again reduced. The grinded and chipped rice straw is finally collected in a tray. The grinded biomass was then sieved by using sieves of different sizes. Mainly to obtain desired particle size, sieves of different size was used. The different sizes of sieves used was 20MIC, 250MIC, 425MIC, 825MIC and 1.2MM. The different types of sieves arranged according to increasing number of their size and then by applying mechanical sieve shaker the biomass were separated into different size as the sizes of the sieves. Seventy five percent by weight of the initial rice straw was retained after the milling and sieving process. The ground and sieved raw material was

stored in air tight plastic bags and kept at room temperature. The materials were used shortly after milling.

Pre-soaking of rice straw in solvents

Pre-soaking in chloroform and hexane

Ten grams of milled and sieved rice straw was soaked in 80ml of chloroform and hexane solution separately. The time interval for soaking was varied from 2hr to 8 hr. 10gm of milled and sieved rice straw was taken in a glass bottle, to that 80ml of chloroform and hexane solution was added and kept at room temperature for 2hr, 4hr, 6hr and 8hr. Each after 2hr, 4hr, 6hr and 8hr the supernatant was collected in a glass vial and stored at 4 °C. immediately after collecting the supernatant the presoaked biomass i.e. rice straw was dried overnight at 50°C in oven. After overnight drying the presoaked biomass (rice straw) was weighed and kept in a air tight plastic container. The biomass (rice straw) was then further used for acid hydrolysis and alkaline hydrolysis. The reaction volume was 100ml for acid hydrolysis. The acid hydrolysis was done at 121°C. sulfuric acid at varying conc. from 1% to 4%. For 100 ml reaction volume 5% lignocellulosic biomass was loaded i.e. 5gm rice straw was loaded to reaction volume and the mixture was employed at 121°C for 1hr. After heat treatment the mixture was filtered through muslin cloth and the supernatant was collected in vials/centrifuge tube (50ml). The biomass (rice straw) was then dried overnight in oven at 50 °C. after overnight drying the biomass is weighed and subjected for compositional analysis

Alkali Treatment

The alkali added was 2% of the total reaction volume and the biomass loading was 5% of the total reaction volume. Mainly to optimize the alkaline pretreatment the alkali concentration and the temperature was varied. The alkaline pretreatment was carried out at 121°C. For optimization the process the presoaked biomass was employed for the alkaline hydrolysis. In first step of process optimization, the rice straw was soaked in chloroform solution for 2hr, 4hr, 6hr and 8hr. The supernatant was discarded and the biomass was then employed for alkali pretreatment. The reaction volume was 100ml; according to that 2% sodium hydroxide was added. The presoaked rice straw added was 5gm. The reaction mixture with biomass then subjected at 121°C for 1hr. In second step of process optimization, the rice straw was soaked in hexane solution for 2hr, 4hr, 6hr and 8hr. The supernatant was discarded and the biomass was then employed for alkali pretreatment. The reaction volume was 100ml; according to that 2% sodium hydroxide was added. The presoaked rice straw added was 5gm. The reaction mixture with biomass then subjected at 121°C for 1hr. In third step of process optimization, the concentration of alkali was varied. The concentration of sodium hydroxide was varied from 0.5 to 2.5%. In this pretreatment the Biomass loading was 5% of the total reaction volume and the temperature was also constant. The reaction mixture was prepared by varying sodium hydroxide concentration as 0.5%, 1.5%, 2% and 2.5% and one sample was kept as a control (without adding alkali). The Reaction mixture was 100ml, to this reaction mixture 5gm rice straw was added. The whole mixture was then subjected to 121°C for 1hr. The supernatant was then collected and analysed for total reducing sugars and total phenolics. The rice straw was collected by filtering through muslin cloth and dried. The compositional analysis of the collected rice straw is then carried out.

Total reducing sugars assay

Each sample 1ml (10 times diluted) was added to 3 ml of dinitrosalicylic acid. After 1min of mixing, the sample was kept in boiling water bath at 100°C for 5 min. After cooling 0.5ml of sample was taken and 4.5 ml of deionized water was added. The absorbance was measured at 540nm. The aldehyde group of glucose converts 3,5 dinitrosalicylic acid into 3-amino 5-nitrosalicylic acid, which is reduced form of DNS. Water is used up as a reactant and oxygen gas is released during reaction. The formation of 3-amino 5-nitrosalicylic acid results in the change in the amount of light absorbed at 540nm.

Total phenolics assay

Standard calibration curve for Gallic acid was prepared by using standards from 0.1 mg/mL to 0.5 mg/ml. The phenolic content of hydrolysate samples was determined using Folin–Ciocalteu reagent. 0.1 ml of sample (with proper dilution) was added to 2.9ml of deionized water and 0.5ml of Folin-

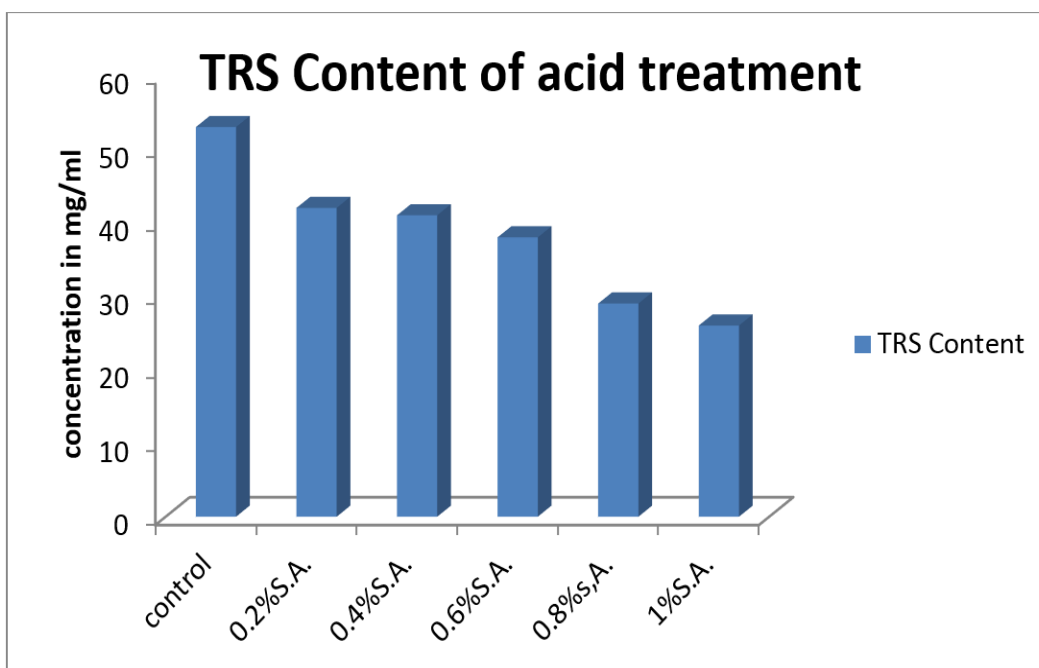
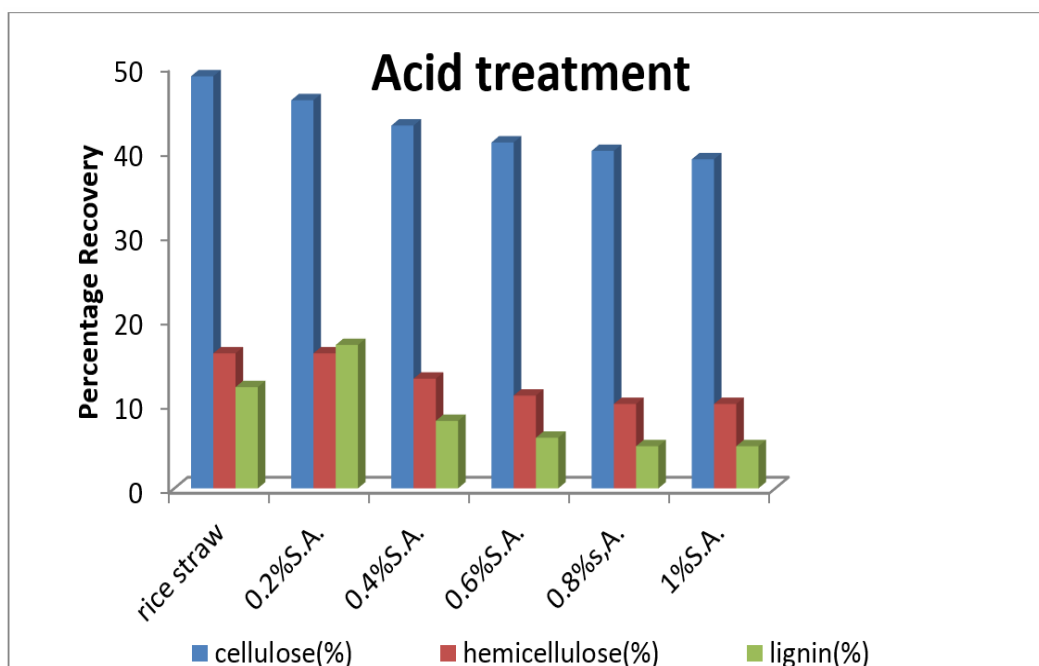
Ciocalteu reagent (Sigma-Aldrich) was added. After 1min of incubation, 2 ml of 20% solution of sodium carbonate was added. In alkaline medium, Folin-Ciocalteu reagent reacts with phenolic compounds to form a blue chromophore constituted by a hosphotungstic/phosphomolybdenum complex where the maximum absorption depends on the concentration of phenolic compounds. The mixture was incubated for 3 min at room temperature in the dark and was kept in boiling water bath at 100°C for 1 min and the absorbance was measured at 650 nm

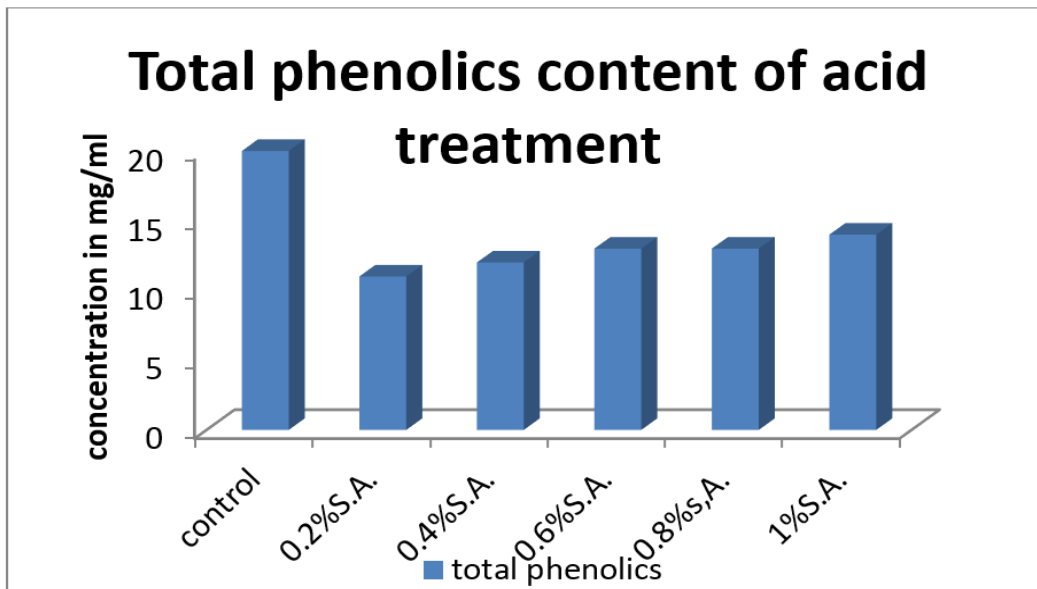
Compositional analysis

The compositional analysis of rice straw was carried out by using NREL (National Renewable Energy Laboratory) protocol.

Result and discussion

Acid treatment

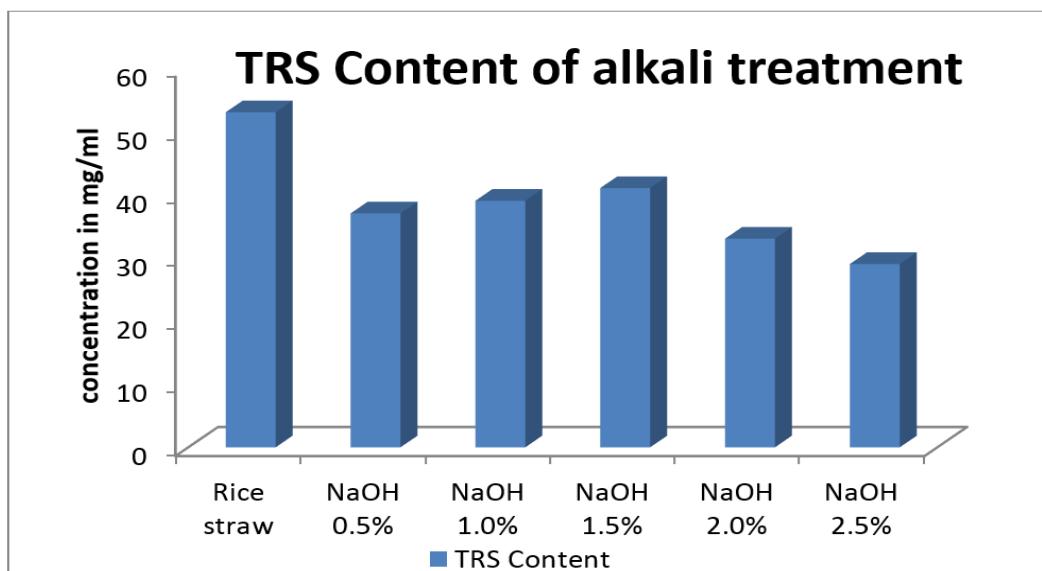
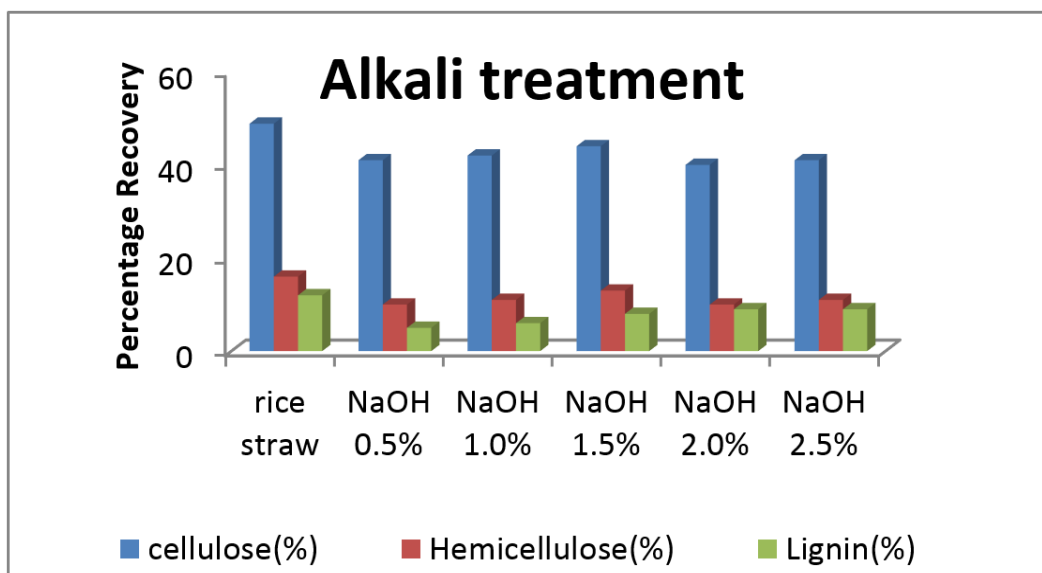


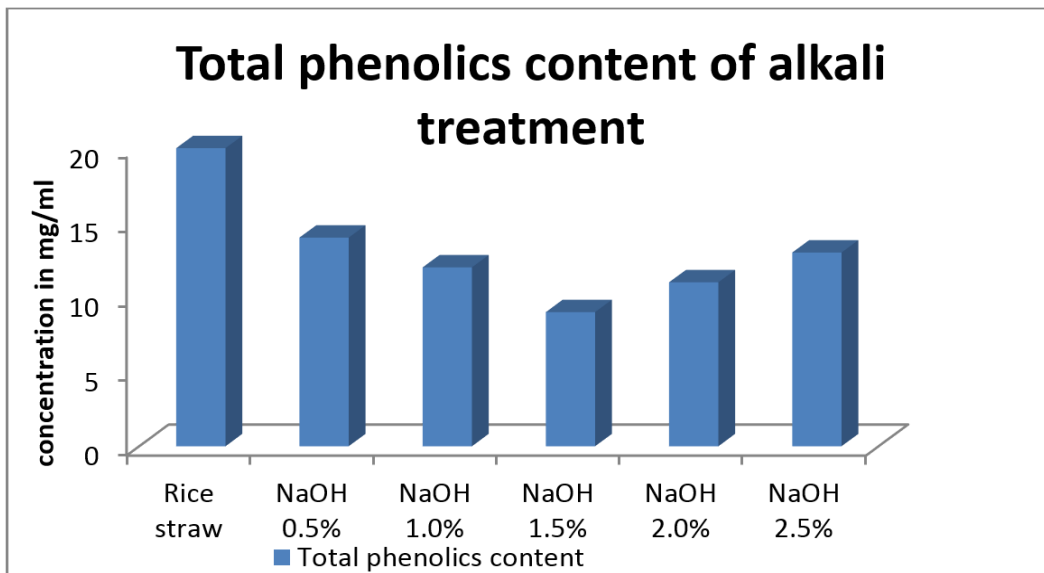


In acid treatment, highest amount of hemicellulose and cellulose content was found in the biomass treated with 0.2% sulfuric acid. There is no significant effect on hemicellulose and cellulose yield by increasing the concentration of sulfuric acid above 0.2% for treatment. Highest amount of total

reducing sugars and lowest amount of total phenolics content was found in liquid of biomass treated with 0.2% sulfuric acid, 0.2% sulfuric acid was found to be most effective.

Alkali treatment

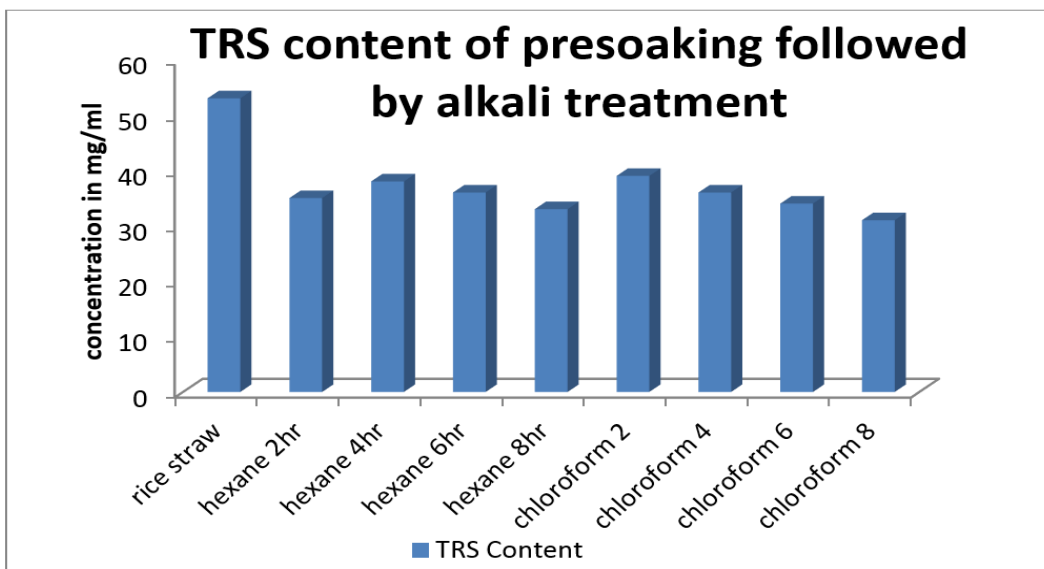
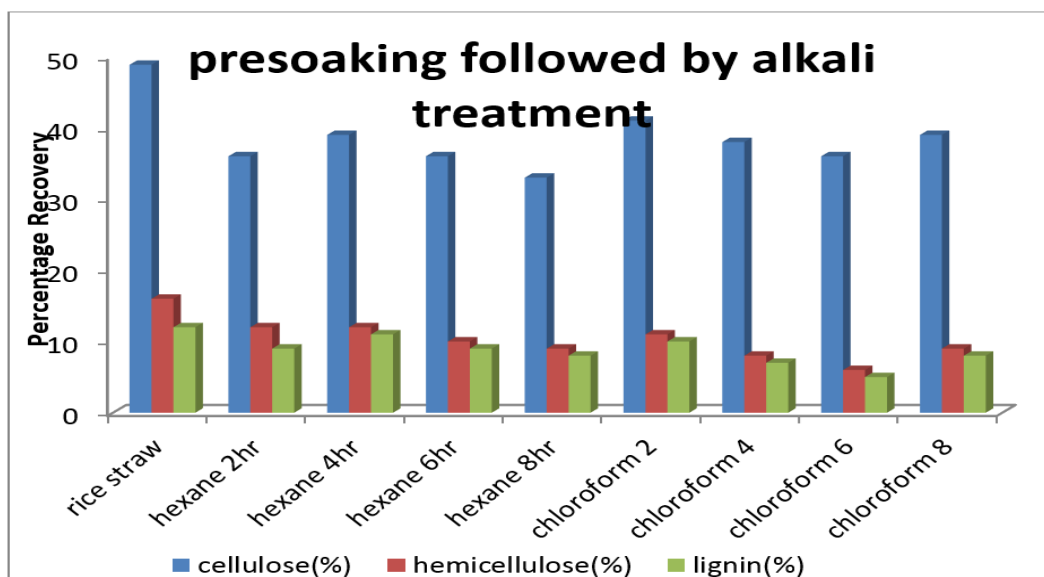


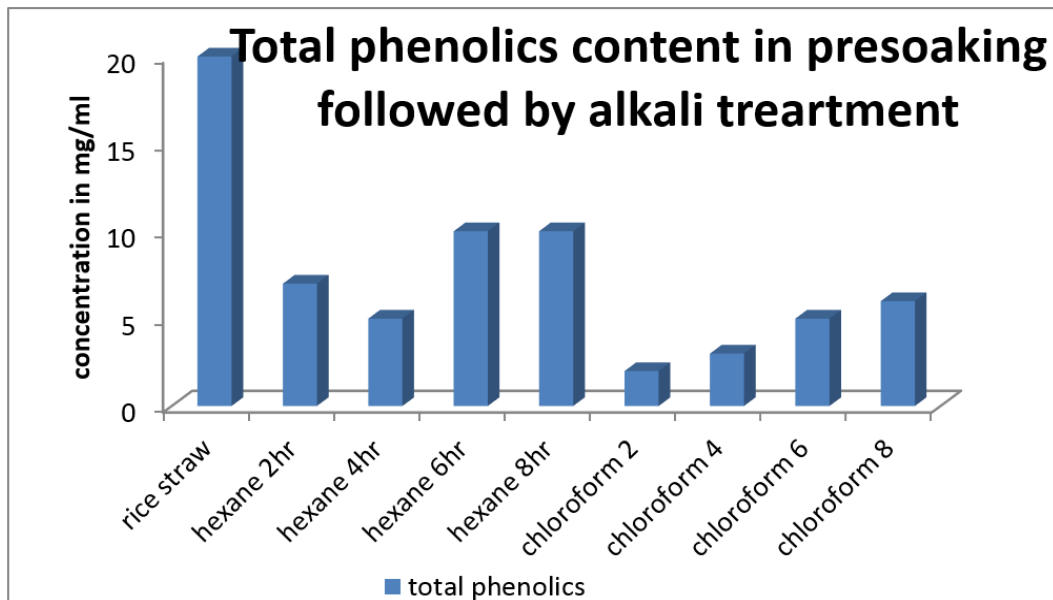


In alkali treatment, highest amount of hemicellulose and cellulose content was found in the biomass treated with 1.5% sodium hydroxide. There is no significant effect on hemicellulose and cellulose yield by increasing the concentration of sodium hydroxide above 1.5% for treatment. Highest amount of total reducing sugars and lowest amount of

total phenolics content was found in liquid of biomass treated with 1.5% sodium hydroxide, 1.5% sodium hydroxide was found to be most effective.

Pre-soaking followed by alkali treatment





In pre-soaking followed by alkali treatment, highest amount of hemicellulose and cellulose content was found in the biomass presoaked in hexane for 4hr and in chloroform for 2hr and then treated with 1.5% sodium hydroxide. There is no significant effect on hemicellulose and cellulose yield by increasing the time of pre-soaking above 4hrs for hexane and above 2 hrs for chloroform, for treatment. Highest amount of total reducing sugars and lowest amount of total phenolics content was found in liquid of biomass pre-soaked in hexane for 4hrs and in chloroform for 2hrs treated with 1.5% sodium hydroxide. Pre-soaking in chloroform for 2hrs and in hexane for 4hrs followed by alkali treatment was found to be most effective.

Conclusion

In acid treatment, 0.2% sulfuric acid was found to be most effective treatment. There is no significant effect on hemicellulose and cellulose yield by increasing the concentration of sulfuric acid above 0.2% for acid treatment. In alkali treatment, 1.5% sodium hydroxide was found to be most effective treatment. There is no significant effect on hemicellulose and cellulose yield by increasing the concentration of sodium hydroxide above 1.5% for alkali treatment. In pre-soaking followed by alkali treatment, pre-soaking in hexane for 4hrs was found to be most effective treatment. In pre-soaking followed by alkali treatment, pre-soaking in chloroform for 2hrs was found to be most effective treatment.

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