

Preparation and Characterization of Thiourea-Silica Hybrid as Heterogeneous Catalyst

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Sodium silicate was prepared from rice husk ash (RHA), which then functionalized with 3-(chloropropyl)triethoxysilane *via* simple sol-gel technique to form RHACCl. The chloro group in RHACCl was replaced in iodo group to form RHACI. Thiourea was immobilized on RHACI to synthesize nanoheterogeneous catalyst labeled as RHATU-SO₄H. The FT-IR analysis clearly indicated the presence of primary amine -NH₂ and C-N absorption band. BET surface area measurement also showed that the surface area is 357 m²/g of catalyst with pore size distribution (2-20 nm) which falls within the mesoporous region. The elemental analysis has also proved the existence of nitrogen and sulfur in the structure of the catalyst. Upon application of RHATU-SO₄H as a catalyst, the degradation of cellulose to glucose yields 81 % at 140 °C for 16 h. The synthesized catalyst is easy to synthesize, highly stable throughout hydrolysis of cellulose as well as reusability without loss of catalyst activity.

Keywords: Rice husk ash, Thiourea, Hydrolysis of cellulose, Glucose.

INTRODUCTION

The rice covers 1 % of surface area of the earth which represents one of the first sources of food for billions of persons [1]. The global badly rice production has been estimated to be 750 million ton in 2015. This amount may produce around 150 million ton of rice husk [2]. Rice husk (RH) is a by-product of rice milling industry [3]. Rice husk produced ash has a high silica content of about 90-95 % after completion combustion at 500-800°C [4]. Precisely, it is considered as a natural and a prefect source of amorphous reactive silica, which is employed as inorganic, support for heterogeneous catalysts [5]. The immobilization of 3-chloropropyltriethoxysilane (CPTES) onto rice husk ash (RHA) extracted silica as hybrid organic-inorganic materials have unique properties due to the high surface area and the presence of the organic functional group (CH₂-Cl) [6]. Pérez-Quintanilla *et al.* [7] immobilized CPTES onto rice husk ash in a simple method followed by the nucleophile replacement of the chlorine by organic part.

Cellulose is bioorganic molecule with a long linear chain polymer of the several monomeric D-glucose units linked by β-1,4-glycosidic bonds. It is the most abundant organic compound in nature does exist in the cell wall of plants as complex fibrous carbohydrates [8]. Moreover, cellulose molecule is linear chain including of 1-1000 million D-glucose units. The degradation of cellulose is quite difficult to be achieved [9] but it has become easier through using enzyme, concentrated

acid and ionic liquid [10]. Microorganism in nature is well-known in the oroduction of soluble sugar, primarily cellobiose and glucose [11].

EXPERIMENTAL

Sodium hydroxide (BHD, England 99%), nitric acid (CDH, India 70 %), 3-chloropropyltriethoxysilane (Sigma, Garmin 99 %), thiourea (Sigma, Germany 99%), toluene (GCC, England 98 %), DMSO (GCC, England 97 %), triethylamine (CDH, India 98 %), ethanol absolute (99 %), methanol (99 %), DMF (LOBA, Cheme 99.8%). All the chemicals used were of AR grade or a high purity and used directly without further purification.

Extraction and modification of silica from RHA

Source of silica: The RHA was chosen as an amorphous silica source, it is available in the profusion. The silica was extracted from rice husk as described in the literature [12,13].

Functionalization of RHA with CPTES: According to the procedure described in the reference [14], 3 g of RHA was placed in 200 mL of 2 M NaOH in a plastic container at 75 °C for 60 min. The produced sodium silicate was filtered to get rid of the undissolved particles. A 6.0 mL solution of CPTES was added to the prepared sodium silicate solution. This solution was added dropwise (1.0 mL/min) to 3.0 M of nitric acid with constant stirred. The difference in pH was observed by using pH meter. A white gel started to form when

the pH decreased to less than 11, the titration was continued until the pH of the solution reached up to 3.0. The obtained gel was aged for 2 day in a covered plastic container. After 2 days, the aged gel was washed six times with distilled water and centrifuged at 4000 rpm for 8 min. The final washing was achieved with acetone and then dried at 100 °C. Finally, the formed precipitate was grounded to produce a final powder. this sample was labeled as RHACCl [14].

Iodide-exchanged polymers: 1 g of the polymer RHACCl was suspended in 50 mL dry acetone (50 mL containing 4 g sodium iodide) and the mixture was refluxed for 60 h. The formed solid precipitate was then filtered off, washed with water, methanol and ether and dried *in vacuo* at 100 °C [15], this sample was labeled as RHACI.

Functionalization with thiourea: 2 g (0.026 mmol) of thiourea (TU) was dissolved in dry toluene (30 mL) and mixed with 1.0 g of RHACI. Then, 3.79 mL (0.026 mmol) Et₃N was added and the mixture refluxed at 110 °C in an oil bath for 24 h (**Scheme-I**). The solid phase was filtered and washed with DMSO, DMF and then ethanol. The precipitate was then dried at 100 °C for 24 h [16]. Finally it was grounded to form fine powder. A 0.85 g product was collected and then 2.0 g of the RHATU was stirred in the 40 mL of 0.5 M sulfuric acid at room temperature for 24 h to form thiourea sulfate catalyst RHATU-SO₄H. The formed solid precipitate was filtrated, washed with distill water and dried at 100°C for 24h [17].

Cation exchange capacity (CEC) of the catalyst: 1 g (17 mmol) sodium chloride was dissolved in 25 mL distilled water in a conical flask with stirring. 1 g of RHATU-SO₄H was added to mixture and left for 30 min. After that 2-3 drops of phenolphthaline was added to the reaction mixture and titrated against standard sodium hydroxide solution. Three separated titration was performed an average value for the CEC of RHATU-SO₄H.

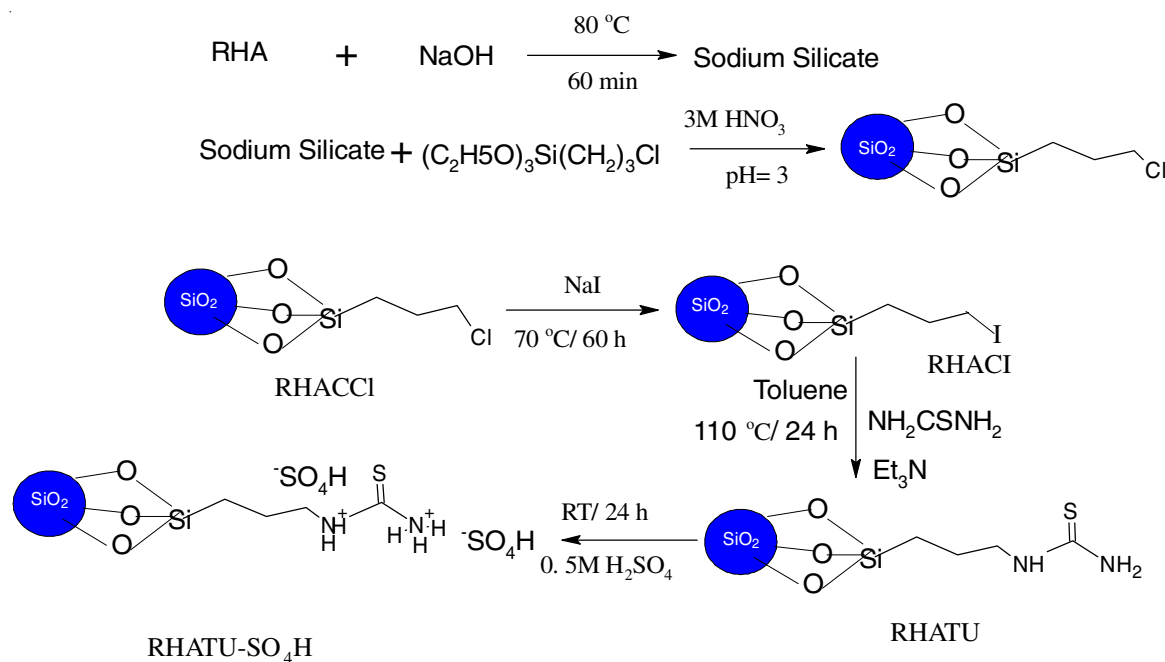
Catalytic hydrolysis procedure: The hydrolysis of cellulose was carried out in 250 mL round bottom flask equipped

with magnetic stirrer and water condenser. 200 mg LiCl, 30 mL DMF and 180 mg cellulose were separately transferred to the round bottom flask containing the catalyst (which dried at 110 °C for 24 h and cooled in desiccator to minimize moisture content). The degradation temperature was adjusted to 140 °C. The hydrolysis suspension was refluxed for 14 h. A 0.5 mL of clear mixture of the hydrolysis suspension was transformed into vial and 2 mL of deionized water was added and the mixture was put in the water bath at 90 °C for 10 min. The blank sample was prepared with 0.5 mL of DNS and 2 mL deionized water and heated under same conditions of the sample. The absorbance of the sample was measured at 450 nm against the blank and the glucose concentration were calculated by using a standard curve of glucose.

Sample characterization: The prepared RHATU-SO₄H was characterized by elemental analysis (Eager 300 for EA1112), thermogravimetric analyses (TGA DTG, Q50 V6.3 Build 189), from 30 to 600 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow. Powder X-ray diffraction (Siemens Diffractometer D5000, Kristalloflex), nitrogen adsorption porosimetry (Belsorp Adsorption/Desorption Data Analysis Software BEL Japan, Inc.), FT-IR spectroscopy (FT-IR-8400 S shimadzu (Japan)), scanning electron microscopy (SEM) ([EDS]-Hidch SU 750, Oxford instruments).

RESULTS AND DISCUSSION

Infrared spectroscopy of analysis: Figs. 1 and 2 show the FT-IR spectra of RHACI and RHATU-SO₄H, respectively. The broad band about 3445 cm⁻¹ is generally attributed to O-H stretching vibration from SiO-H and HO-H of absorbed onto surface of silica. The band about 1631 cm⁻¹ represents the HO-H bending vibration. The band around 3188 and 3325 cm⁻¹ belongs to stretching primary -NH₂ symmetric and asymmetric. The band around 2959 cm⁻¹ assigned to stretching vibration of CH₂. While the bending vibration of the CH₂ group appearance in 1448 cm⁻¹. The band of C-N can be seen at 1541 cm⁻¹. The Si-C



Scheme-I: Synthesis of catalyst RHATU-SO₄H

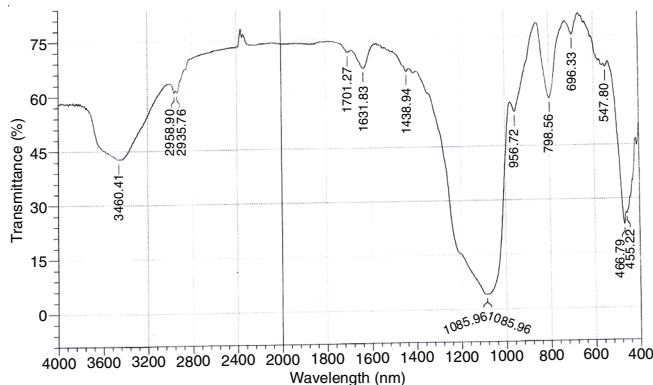
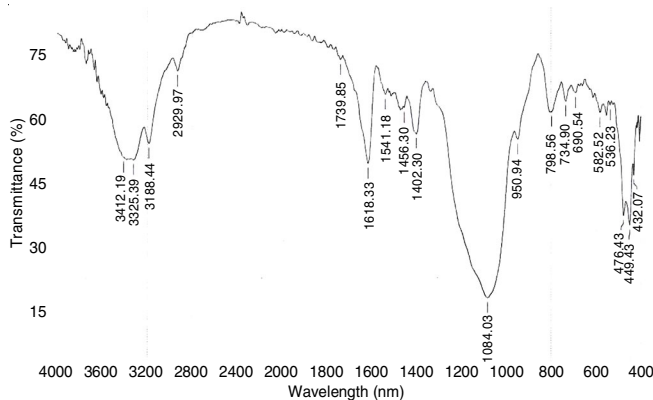


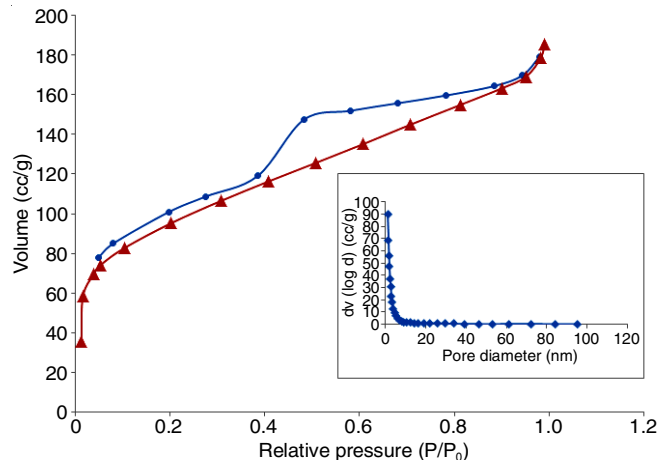
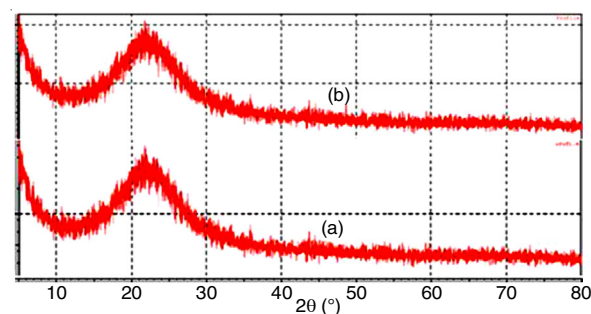
Fig. 1. FT-IR spectrum of RHACI

Fig. 2. FT-IR spectrum of RHATU-SO₄H

vibration was observed at 1273 cm⁻¹ [6]. The FT-IR spectrum of RHATU-SO₄H also appeared a broad stretching vibration of the Si-O-Si compared with narrower band of Si-O-Si in RHACI. The new bands and changes in some bands in FT-IR spectrum of RHATU-SO₄H portrays a good evidence for the successful functionalization of RHACI with thiourea [18].

Nitrogen adsorption-desorption analysis: The surface area analysis of RHATU-SO₄H was measured by the nitrogen adsorption-desorption. Fig. 3 shows the N₂ adsorption-desorption isotherm and EJD distribution of pore size for RHATU-SO₄H. IUPAC classification of the isotherm for RHATU-SO₄H is in agreement with the type IV and H₂ hysteresis loop [19]. It can be seen in Fig. 3 that the nitrogen adsorption isotherm of RHATU-SO₄H gave a hysteresis loop observed in the range of 0.4 < P/P₀ < 1.0 which is associated with capillary condensation according to IUPAC classification. The BET analysis also showed that the specific surface area of the RHATU-SO₄H was 357 m²/g whereas specific surface area of RHACI was 633 m²/g. The decrease in the surface area of the RHATU-SO₄H could be due to the fact that the immobilization of thiourea on the silica surface was blocked some of the pores. RHATU-SO₄H has pore size distribution (2-20 nm) which falls within the mesoporous region.

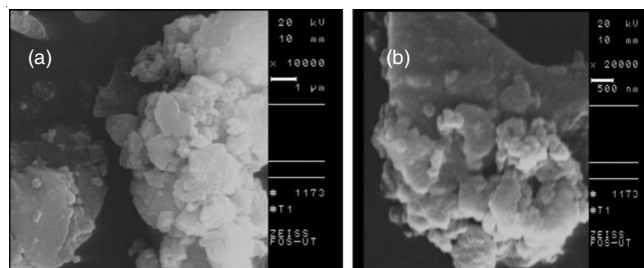
Powder X-ray diffraction pattern: Bui *et al.* [20] reported that XRD patterns of RHA had a phase transfer of RHA to be amorphous silica in the temperature ranged from 300 to 700 °C. Fig. 4 has demonstrated XRD patterns for RHACI and RHATU-SO₄H which stated a broad diffraction band at 2θ angle of about 22°. These results are typically corresponding with XRD patterns of amorphous silica of RHACI and RHATU-SO₄H [21].

Fig. 3. Nitrogen adsorption-desorption for RHATU-SO₄HFig. 4. Powder X-ray for (a) RHACI and (b) RHATU-SO₄H

Elemental analysis (CHNS): The CHNS analysis was estimated for RHACI and RHATU-SO₄H. This analysis have showed successful incorporation of thiourea on RHACI. Table-1 shows the elemental data analysis of RHA, RHACI and RHATU-SO₄H. The elemental analysis of RHACI explained that the C% and H% was 11.7 and 1.90 %, respectively [22], while elemental analysis of RHATU-SO₄H indicated the presence of N and S in addition to C and H. Thus, these results obviously indicated the successful immobilization of thiourea onto RHACI.

TABLE-1				
Sample	C (%)	H (%)	N (%)	S (%)
RHACI	11.70	1.90	—	—
RHATU-SO ₄ H	13.18	2.96	1.44	8.96

Scanning electron microscope (SEM): The scanning electron microscope (SEM) images of the RHATU-SO₄H are shown in Fig. 5. It seems that the surface of RHATU-SO₄H similar to some rocky particle with shaped shell that randomly distributed onto surface.

Fig. 5. SEM of catalyst RHATU-SO₄H (a) 1 μm (b) 500 nm

Thermogravimetric analysis (TGA/DTG): The thermogravimetric analysis TGA/DTG was performed in the range of 25 to 600 °C at the heating rate of 10 °C/min. Fig. 6 designates to TGA of the RHATU-SO₄H that showed two characteristic decomposition stages. The initial step appeared mass loss (about 2.015 %) at around 25-120 °C. This loss is attributed to the absorbed water onto surface of silica. The second mass loss (about 37.25.0 %) occurred between 250 to 460 °C and it seems to be degradation of propylthiourea moieties [23]. Additionally, The DTG analysis for the RHATU-SO₄H is shown in Fig. 7. The thermal decomposition of RHATU-SO₄H has displayed two main weight loss steps. These two steps of DTG are in accordance with the results obtained from DTA in terms of the thermal decomposition of water absorbed onto surface of silica and alkyl thiourea group [24].

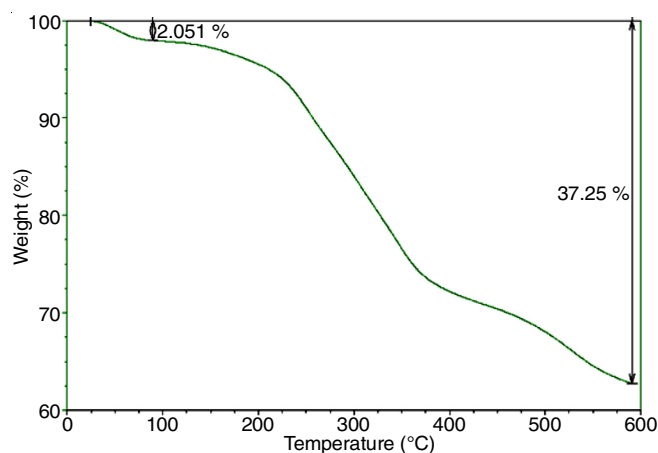


Fig. 6. TGA curve of RHATU-SO₄H showing two mass loss

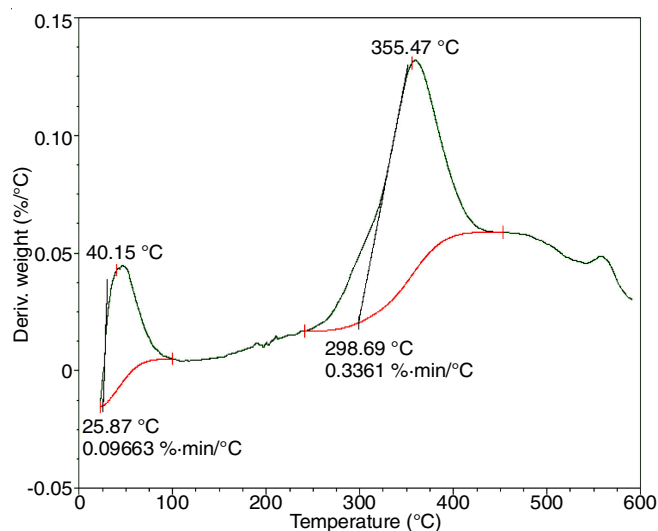


Fig. 7. DTG of RHATU-SO₄H show two thermal degradation

Surface acidity of RHATU-SO₄H: A general perception is that surface acidity can be linked to catalyst activity. Many spectral and thermal methods can be used for the characterization of the surface of solid catalyst. The location of acid distribution on the RHATU-SO₄H was determined in water. The excess Na⁺ (from NaCl) with acid proton were titrated with standard NaOH solution. the exchange of cation capacity (CEC) was found 15 mmol/100 g of catalyst [3].

Hydrolysis of cellulose: The heterogeneous catalyst activity *i.e.* RHATU-SO₄H and homogeneous thiourea (TU) towards cellulose hydrolysis to glucose were studied. The parameters of hydrolysis such as temperature, mass of catalyst, effect of solvent and reusability of the RHATU-SO₄H catalyst were evaluated to optimize the condition of hydrolysis.

Effect of hydrolysis time: The time effect on hydrolysis of cellulose to glucose by RHATU-SO₄H and homogeneous thiourea (TU) are observed in Fig. 8. The hydrolysis were conducted by using 200 mg catalyst, DMF as a solvent and LiCl at 140 °C. The first degradation of cellulose hydrolysis to glucose was 16 % within the first 6 h and then increased to maximum of 81 % in 16 h. However upon increasing the hydrolysis time (more than 16 h), no change was observed in cellulose hydrolysis. Therefore the optimum time of cellulose hydrolysis over RHATU-SO₄H is 16 h. On the other hand, 200 mg homogeneous (thiourea) showed 27.4% of cellulose hydrolysis for the same period of time. Hence, this thiourea (TU) cannot be used as a catalyst in cellulose hydrolysis into glucose. While heterogeneous thiourea (thiourea functionalized RHATU-SO₄H) is currently much more valuable and should be taken into consideration since it gives reasonably greater hydrolysis.

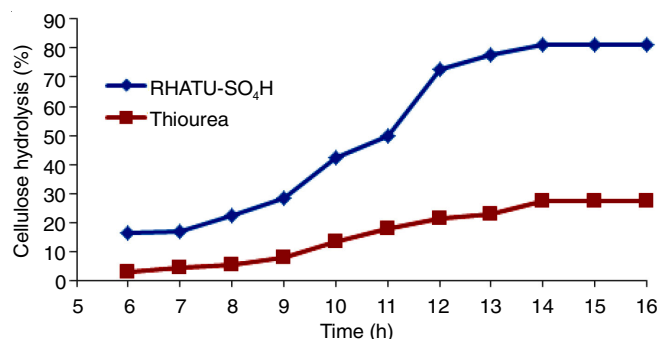


Fig. 8. Hydrolysis of cellulose to glucose over RHATU-SO₄H and homogeneous thiourea as a functional of the hydrolysis time

Influence of catalyst mass: In order to find the best catalyst mass that required to hydrolysis of cellulose, the analysis was carried out by changing the amount of RHATU-SO₄H from (150-250 mg) at fixed hydrolysis temperature at 140°C, time of hydrolysis for 16 h and solvent DMF/LiCl. The results has shown in Fig. 9. It is clearly indicated that as the mass of catalyst increased from 150 to 200 mg, the hydrolysis of cellulose

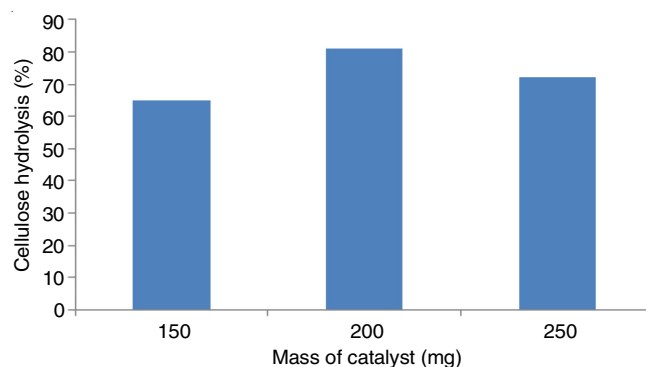


Fig. 9. Relationship between mass of catalyst and the glucose yield on the hydrolysis of cellulose over RHATU-SO₄H

lose into glucose raised from 68 to 81 %. However, no significant influence on cellulose hydrolysis was noticed upon increasing the mass of catalyst. It was found that 200 mg chosen as the optimum value of the RHATU-SO₄H catalyst.

Influence of hydrolysis temperature: Fig. 10 demonstrated the effect of hydrolysis temperature effects on role of RHATU-SO₄H as a catalyst in the cellulose hydrolysis. It clearly observed that the cellulose hydrolysis increased when temperature rises from 120 to 140 °C whereby the hydrolysis increased to 81 % at 140 °C.

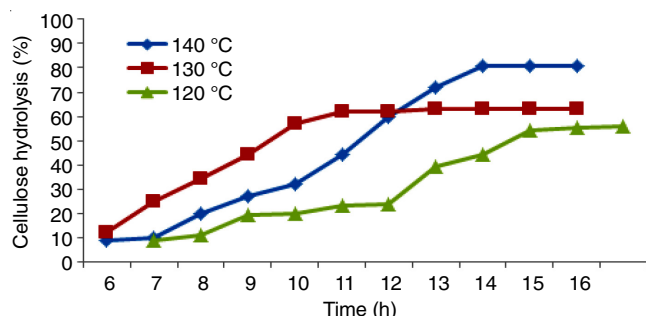


Fig. 10. Conversion of cellulose to glucose over RHATU-SO₄H at different temperature

Influence of solvent: It was also studied the effect of solvent on cellulose hydrolysis into glucose over RHATU-SO₄H as given in Table-2. The condition of hydrolysis was fixed as follows: reaction time 16 h, hydrolysis temperature 140 °C and catalyst mass 200 mg. The solvents used *i.e.* toluene, 3-methylpropan-2-ol and DMF. It was noticed that there was a significant effect in the cellulose hydrolysis by using different solvents DMF > 2-methylpropan-2-ol > toluene. Therefore, the cellulose hydrolysis can be different according to the solubility of the cellulose into different solvents. In this study the cellulose was highly soluble in DMF and 2-methylpropan-2-ol consisting LiCl. Most of our suspension system could form hydrogen bonding between the solvent and layer of cellulose chain. DMF has appeared more solubility of cellulose because of it has more than one center able to form hydrogen bonding with chain of cellulose and this could make the hydrolysis higher and easier in contrast with other solvents that have less solubility of cellulose.

TABLE-2
CELLULOSE HYDROLYSIS TO GLUCOSE OVER
RHATU-SO₄H USE VARIETY OF SOLVENT

Solvent	Conversion of cellulose (m m %)
DMF	81.0
2-Methylpropan-2-ol	55.8
Toluene	44.8

Catalyst recycles: The main advantage of utilization of heterogeneous catalyst is ability to be reused many times. The stability of the catalyst and the activity of its active site are the main parameters of its reuse. Since RHATU-SO₄H is heterogeneous catalyst, hence it was successfully utilized for recycling. In the first hydrolysis it was run by using the catalyst with mixture, and then washed by hot DMF LiCl (this step was repeated three time) and the catalyst heated up to 100 °C for 24 h. Next, fresh cellulose and DMF with LiCl were added to

the catalyst and washed. The consecutive runs were carried out similarly as in above method. As observed in Fig. 11, the results appears in the second and third runs. This product indicated that catalytic performance doesn't lose its activity during the counts of the catalytic runs.

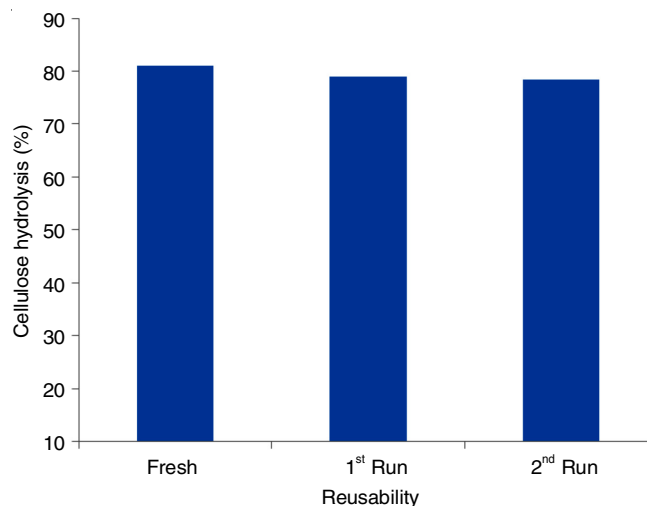


Fig. 11. Reusability of RHATU-SO₄H on the hydrolysis of cellulose

Suggested mechanism for cellulose hydrolysis: The RHATU-SO₄H has acidic sulphate group. These group sites could interact rapidly with the glycosidic oxygen *via* a hydrogen bonding between layers of cellulose chains. Then the cleavage of the C–O bond in the cellulose chains takes place. After that the sulphate group attract the charged species *via* a hydrogen bonding. Finally the yield of monosaccharide after partial hydrolysis is occurred and the catalyst could hydrolyze new cellulose chains as in **Scheme-II**.

Conclusion

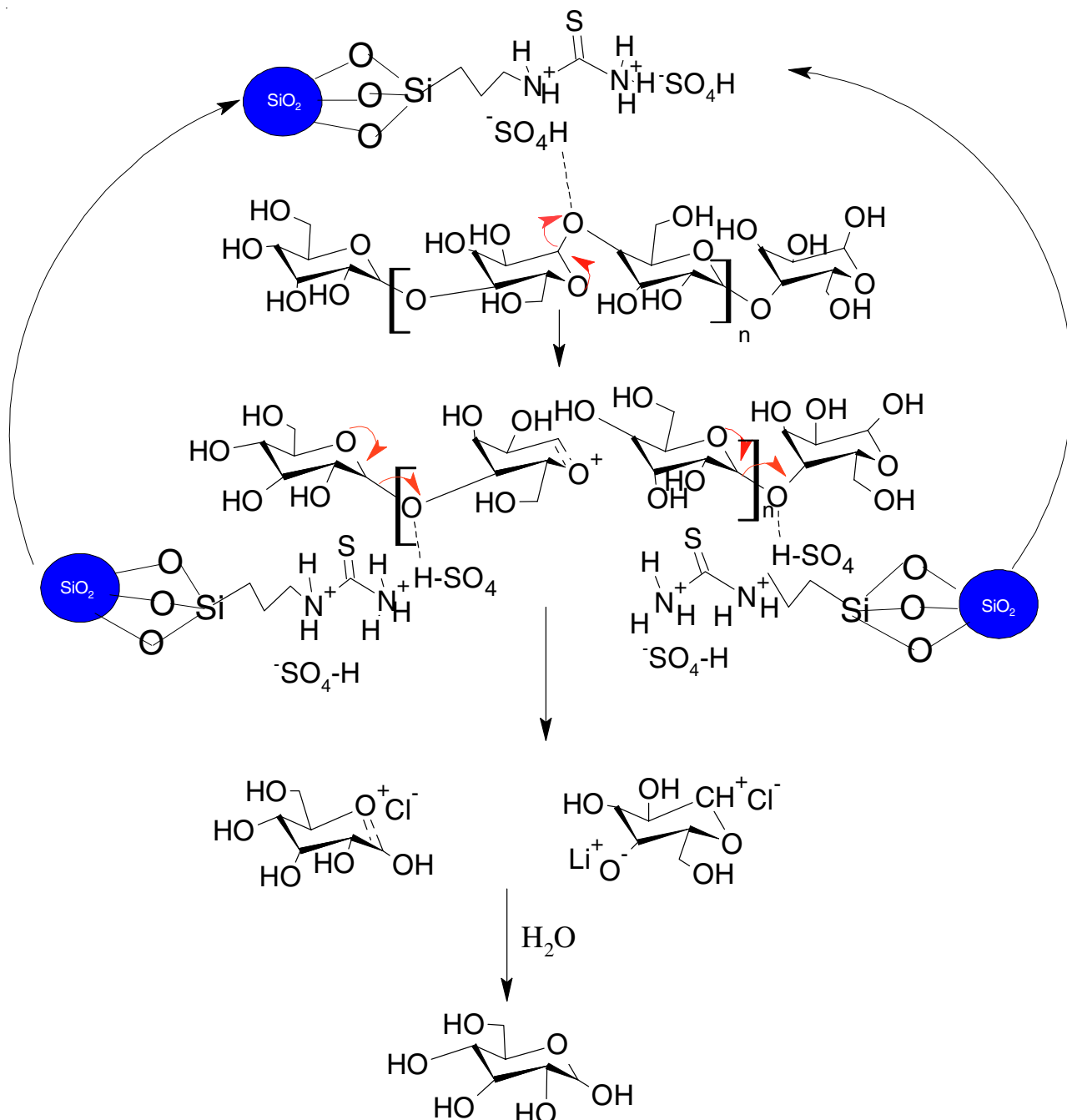
Thiourea was reacted with silica extracted from rice husk ash. The spectroscopic evidence showed the successful synthesis of RHATU-SO₄H. The FT-IR spectrum indicated the presence of primary –NH₂ and formation bond C–N in the catalyst. The N₂ adsorption-desorption study also stated that RHATU-SO₄H has higher specific surface area 357 m²/g. The TGA/DTG indicated the catalyst have two degradation temperature between 25-115 and 260-460 °C. The cellulose hydrolysis, by RHATU-SO₄H to glucose yield 81 % of glucose at 140 °C for 14 h. The catalyst is easy to synthesize, stable, reusable and could be used many times without any activity loss.

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Scheme-II: Suggested mechanism of cellulose hydrolysis to glucose over catalyst RHATU-SO₄H

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