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Synthesis of Sodium-Y-Zeolite from Agricultural Waste Rice Husk Ash and Encapsulated with Copper Metal for Useful Phenol Hydroxylation

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ABSTRACT

Recent days, dumping of natural agricultural rice husk wastes are causing pollution issues due to its lower rate of biodegradation. Also, the rice producing countries are facing problems because of massive amount of rice husk disposal of excess rice husk used for various applications such as energy production, animal feed and charcoal as organic manure in agriculture field. Hence, this work prepared the Copper-Y-Zeolite through Sodium-Y-Zeolite from agricultural waste rice husk for catalytic purpose in organic conversion reaction. The converted Copper-Y-Zeolite (CYZ) was characterized by UV, FTIR, atomic absorption spectra and XRD techniques. Then, it was used as catalyst in Phenol hydroxylation reaction and the reaction outcomes were monitored using high performance liquid chromatography. The optimized reaction condition of 50mg Sodium-Y-Zeolite catalyst encapsulated catalyst with phenol/H₂O₂ ratio (2:1) at 50°C after 6 hours gave good yield. The catalyst efficiency exposed that CYZ may be the good water pollutant adsorbing agent.

Key words: Rice husk, Cu encapsulation, Copper-Y-Zeolite, Catalyst, Phenol hydroxylation

The agricultural excess rice husks are the natural useful byproducts of paddy which creates pollution issues in rice mills after the certain limit [1]. Various studies have shown that the rice husk consists of different chemicals such as silica (15–28 wt %), lignocellulose (72–85 wt %), cellulose (35–40 wt %), hemicellulose (15–20 wt %) and lignin (20–25 wt %) based on the variety, origin, climate, geographic location respectively [2]. Rice Husk Ash (RHA) contains 20% ash comprises 95% of amorphous silica. This amorphous or crystalline silica has the properties such as high surface area, particle size, high purity and high porosity [3] Rice husk is a major waste for low cost silica production. Different Zeolites such as high silica containing zeolite-Y (Si/Al>3) and low silica containing zeolite-X (Si/Al>2-3) are synthesized from RHA [4]. The cation exchanging zeolites are used in various purposes like water and gas

purification, hydrogenating catalysts, isomerization, alkylation and the removal of contaminants (heavy metals, toxic gases, dyes and organic pollutants) [5-9]. Zeolite pore size and acidity can be modified using ion exchange of transition metal. The transition metal ions are exchanged zeolite cages or channels and are act as a good oxidizing agent for phenol hydroxylation instead of Rhone-Poulenc, Brichjma and Ube [10].

Simple metal ions, inorganic cage like molecules including zeolite and metal complexes are the traditional catalysts which are used in various organic chemical reactions [11]. Photography chemicals such as catechol and hydroquinone are applicable in many fields [12]. They are widely used as antioxidants, polymerization inhibitors, pesticides, rubber, textile, steel, petroleum refinery, dye, pharmaceutical, plastic and cosmetic flavoring agents [13]. Both dihydroxy benzenes can be derived from phenol by hydroxylation of phenol along with H₂O₂/CuO [14]. The copper complexes are used as oxidase synthetic models in phenol and catechol oxidation [15] Many kinds of catalysts such as metal oxides, metal complexes, metal incorporated silica, (Fe-MCM-41)₃, zeolites (TS-1) and zeolite-encapsulated metal complexes (Copper(II) phthalocyanines/MFI zeolite catalysts [16-21]. Hence, this work investigated on the objective of excess waste rice husk to useful material for various applications such as catalytic activity and adsorption studies. In this paper, catalytic activity of agricultural paddy waste was investigated.

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Agricultural rice husk ash (RHA) was converted to sodium zeolite in hydrochloric acid and encapsulated with copper oxide for phenol oxidation purpose. The prepared materials were characterized by UV, FTIR, AAS and XRD techniques. The phenol hydroxylation was examined under different operating conditions such as catalyst input, temperature and time. The reaction progress was analyzed by HPLC-DAD which was compared with standards.

MATERIALS AND METHODS

Chemicals and rice husks

All research chemicals were purchased from Sigma Aldrich (Bio corporals, Chennai, Tamil Nadu) and used as such. The 10 kg of natural waste rice husks were purchased from Tirupati, Andhra Pradesh, India.

Instruments

The prepared Sodium Y Zeolite and copper-Y-Zeolite were characterized by Agilent 5000 UV-VIS NIR Spectro photometer. FT-IR was documented as KBr pellet in Shimadzu IR affinity IS (DLATGS detector). XRD of the materials was recorded using Bruker AXS, Diffractometer D8. Atomic absorption spectrum was recorded using Labtronics atomic absorption spectrophotometer. The standard and reaction products were confirmed by Shimadzu make Agilent 1200 series quat pump HPLC.

Synthesis of sodium-Y-Zeolite and Copper-Y-Zeolite

Initially the rice husk was washed with plenty of water to remove the dust and dried at 110°C for 12h. It was treated with 3mol/L hydrochloric acid for 24 hours to

increase the purity of silica and again washed with plenty of distilled water up to the pH = 7.01. After the washing, they were dried at 100°C for 4 h and were burnt at 700°C for 4h in the muffle furnace. 100% combusted whitish color of rice husk ash contains pure silica. The derived silica was converted to sodium silicate solution by treating the rice husk ash with 2M NaOH aqueous solution at 80°C for 5 h with continuous stirring. The solution was filtered under vacuum and the insoluble were removed for the zeolite preparation. The sodium aluminate solution was prepared by adding aqueous 2M NaOH solution to aluminum hydroxide Al (OH) 3 powder. The solution was heated to boiling at 60°C for 4 h [22]. The sodium silicate solution and sodium aluminate solutions were mixed slowly with continuous stirring at 60°C for 5 h to get the sodium aluminosilicate gel. This reaction mixture was then charged into the autoclave for hydrothermal reaction at 100°C with autogenic pressure and left as such for ageing. After the hydrothermal reaction, the prepared powder was collected by centrifugation (6000rpm) followed by repeated distilled water washing until the pH = 7 in digital pH meter. The washed powders were dried at 120°C for 12 hours. The overall process scheme has presented in (Fig 1). The prepared sodium-Y- zeolite treated with 0.1M NH₄NO₃ aqueous solution and stirred at 80 °C for 8 h. the reaction mixture was filtered and washed with water. The obtained NH₄-zeolite was dried in air at room temperature. Then, it was treated with CuSO₄ solution and was stirred in an oil bath at 80°C for 1 h. Then, the reaction mass was filtered under vacuum and washed with deionized water. The resulting Cu-Y-zeolite (CYZ) was dried at 120°C for 8 h. The obtained product was calcinated at 500°C for 8 h in air (Fig 1).

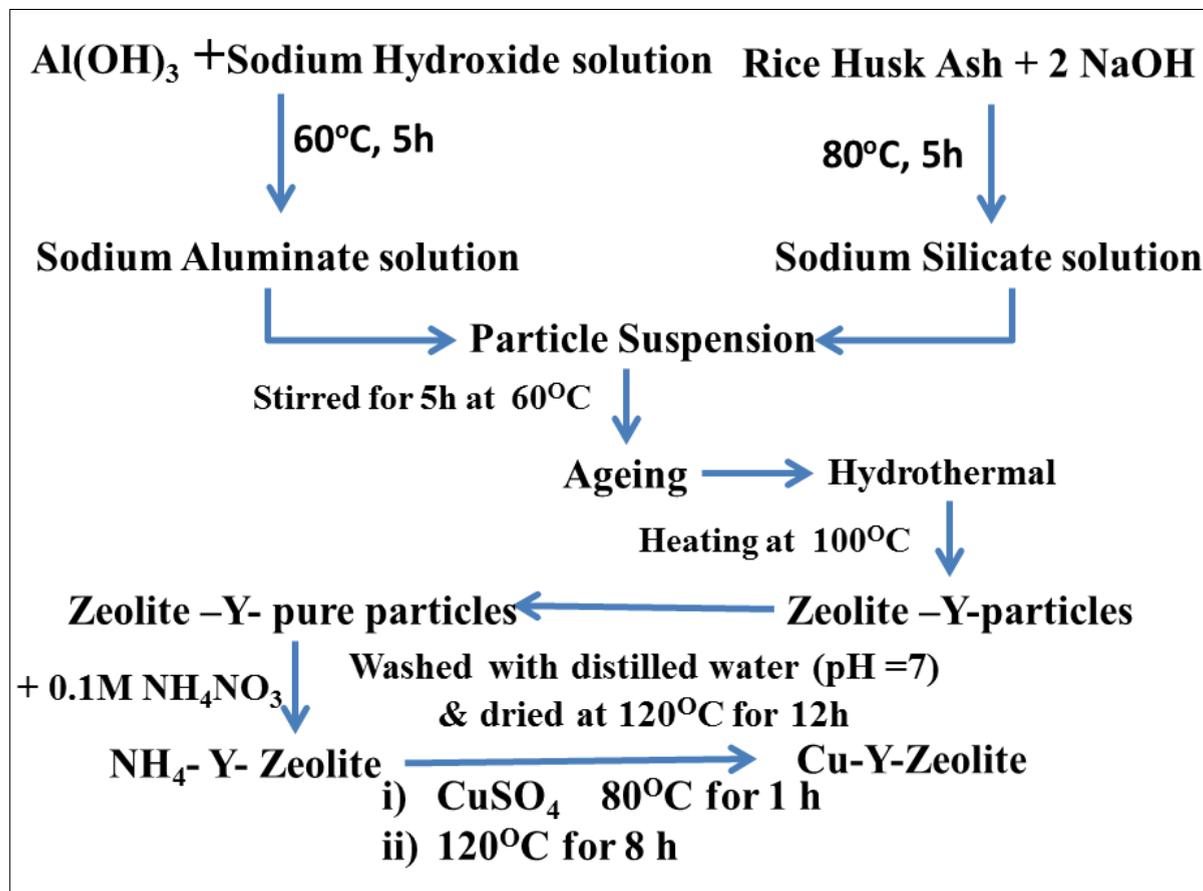


Fig 1 Sodium Y Zeolite and Cu-Y-Zeolite preparation scheme

The obtained CYZ product was characterized by UV, Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), Scanning Electron microscopy (SEM), AAS and Energy dispersive X-ray (EDAX) techniques.

Hydroxylation of phenol in presence of CYZ and H_2O_2

Hydroxylation of phenol was conducted using phenol and hydrogen peroxide (30 wt% water solution, POCH

Gliwice) as per the reported method with small modifications in catalyst [23-24]. Hydroxylation of phenol (Fig 2) was carried out in a stainless-steel autoclave equipped with a 60 cm³ capacity PTFE. Raw materials were introduced into the reactor one by one like catalyst, phenol, and hydrogen peroxide. The reactor was located in a shaker holder and immersed in an oil bath (the intensity of stirring of 300 rpm). The bath temperature was controlled by a thermostat. After completing the reaction, the autoclave was cooled and weighted.

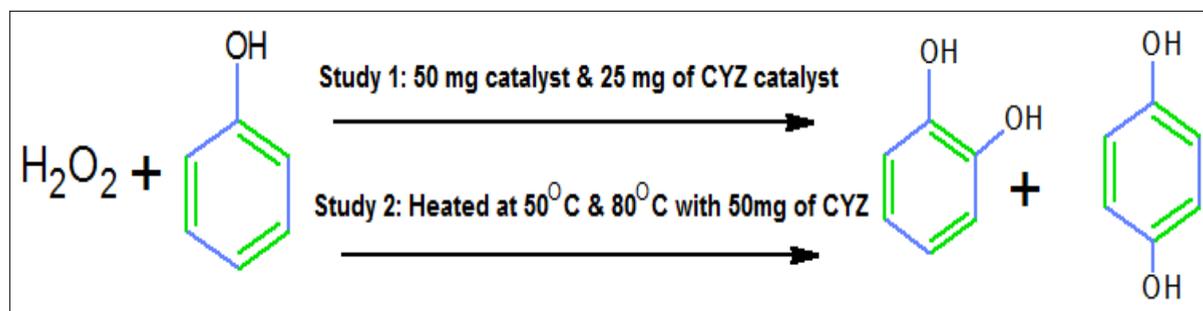


Fig 2 Hydroxylation of phenol using CYZ with different conditions scheme

Catalyst evaluation

Accurately weighed 25 mg and 50 mg of CYZ were treated in 25 ml acetic acid in separate RB flasks which were sonicated for 30 min. After 30 minutes, 10 mmol of phenol was added to each flask and stirred for 45 min. To the reaction mass, 5mmol of 30% hydrogen peroxide was added and were stirred for 6 hours at 50°C. The aliquot samples were collected at the time intervals of 0, 1h, 4 h and 6 h from each flask. All the samples were injected in to a HPLC-DAD system and the products were compared with the standard.

Time duration evolution

Two set of reactions were conducted with 50 mg CYZ in 25 ml acetic acid using similar like catalyst evaluation procedure. The reaction masses were stirred for 6 hours and 8 hours at 50°C respectively. After the time period, reaction products were analyzed using HPLC-DAD system.

Characterization

Absorption and vibrational spectra

The prepared sodium and copper zeolites were analyzed by UV differential reflectance spectroscopy (UV-DRS) between the range of 190 nm and 800 nm. Recorded outcomes were processed using origin pro software. Similarly, vibrational spectra of the prepared two zeolites were recorded between 400cm⁻¹ and 4000cm⁻¹ using KBr pellets.

Atomic absorption spectra

The obtained calcinated CYZ catalyst was characterized by atomic absorption spectroscopy to confirm the presence of Cu and compared with the reported values.

X-Ray diffraction spectra

Both the prepared sodium zeolite and copper zeolites solid nature was analyzed by X-Ray Diffraction spectra.

High performance liquid chromatography (HPLC)

Agricultural waste rice husk-based bio catalyst CYZ used chemical reactions kinetics at the proper intervals were analyzed reverse phase system using methanol and water (40: 60 ratio).

RESULTS AND DISCUSSION

Agricultural rice husk ash waste is successfully converted to oxidizing heterogeneous catalyst copper zeolite (CYZ) as per the reported method with slight modifications [25]. Initially, the CYZ absorption spectrum was recorded to confirm the prepared material with the reported material [25-26]. The recorded DRS-UV exposed the peaks at 203 nm, 211nm and 233 nm respectively (Fig.3a). Absorption spectra of the copper in zeolites exhibited an intense broad band at 200-340 nm and weak band at 360-370 nm. The weak band is related to the d-d transition of Cu²⁺ ions in zeolite structure. The absorption value was coincidence with the reported absorption spectrum of Cu_{0.08}[Si₂₅Al]-MFI [25]. After the basic confirmation, the samples were carried for XRD analysis. X-ray analysis showed the peaks of 2θ at 6.4, 14.6, 30.56, 32.1, 33.5 and 47.5. The material pattern has the h, k, l values such as (0, 0, 2), (1, 1, 1), (2, 0, 2), (1, 1, 3), (3, 1, 1) and (1, 1, 3) which is coincidence with reported C2/c point group [27-28]. The pattern exhibits the good purity (Fig 3b).

Further, the obtained copper zeolite was characterized by FTIR vibrational spectroscopy for the CYZ cage impurity analysis. The stretching and bending vibrations are observed in the range of 300 – 1300 cm⁻¹ which indicates that SiO₄ and AlO₄ linkage. Weak bands were observed for Si–O₃–H–Al at 3565 cm⁻¹ (Fig 4a). The Si–OH–Al groups are exposing into super cages which represents the acidic and homogeneous nature of the CYZ [28]. Then, the prepared material atomic absorption spectrum was analyzed to confirm the composition atoms (Fig 4b). The atomic absorption spectrum of CYZ confirmed the copper at 324.6nm and sodium presence and its purity.

After the characterization and confirmation of the copper zeolite catalyst, the catalyst was carried for the hydroxylation of phenol. Before of the hydroxylation, the

standard phenol and its hydroxylation products standard were injected and their areas with retention time details were recorded. The reverse phase column HPLC chromatograms of standards are presented in (Fig 5a-d). Then, the

agriculture-based biocatalyst carried for the phenol hydroxylation by changing two parameters such as catalyst weight (25 mg and 50 mg) and 50 mg catalyst with different time management.

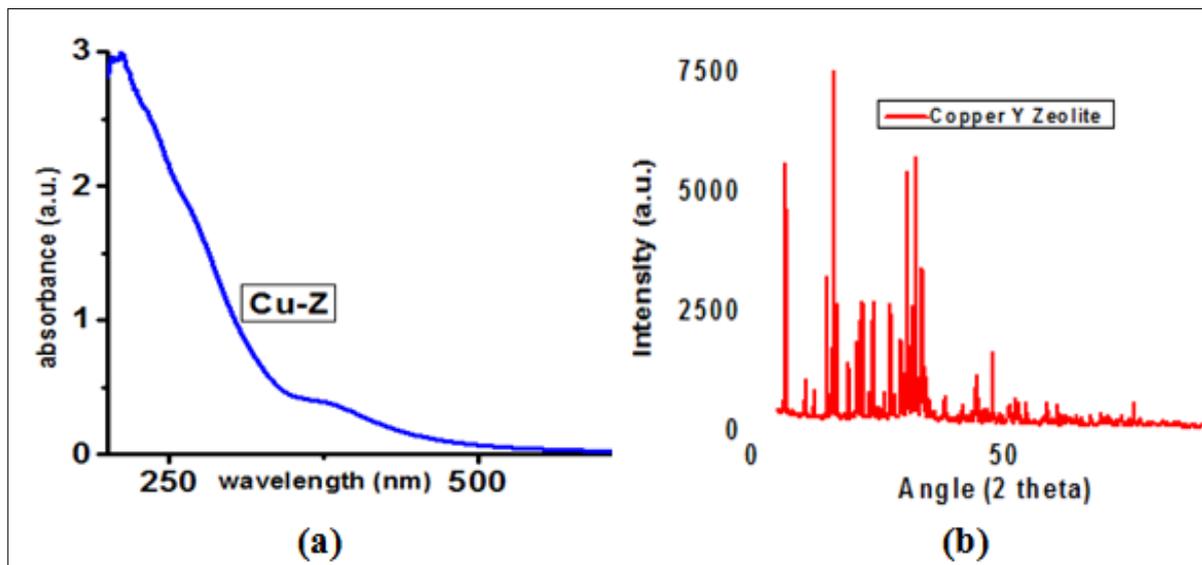


Fig 3 (a) DRS-UV and (b) XRD of CYZ of RHA

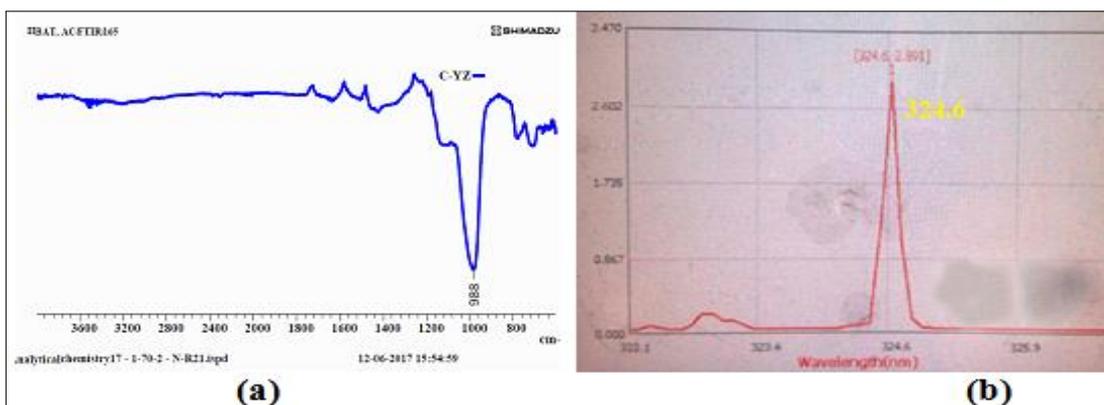


Fig 4 (a) FTIR and (b) atomic absorption spectra of CYZ of RHA

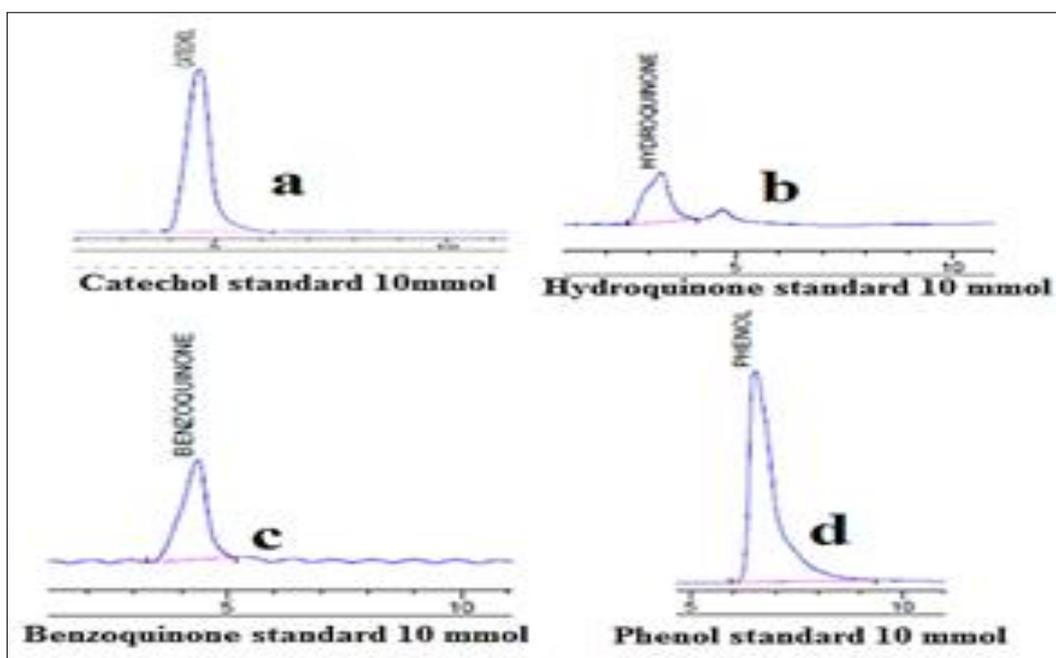


Fig 5 HPLC of standard (a) Catechol, (b) Hydroquinone, (c) Benzoquinone and (d) phenol

Two reactions were conducted using 25mg and 50 mg CYZ catalysts in phenol hydroxylation reaction. The reaction aliquotes were analysed through HPLC and

compared with the standard HPLC area. The HPLC results of differet time intervals and prologed time are presented in (Fig 6-7).

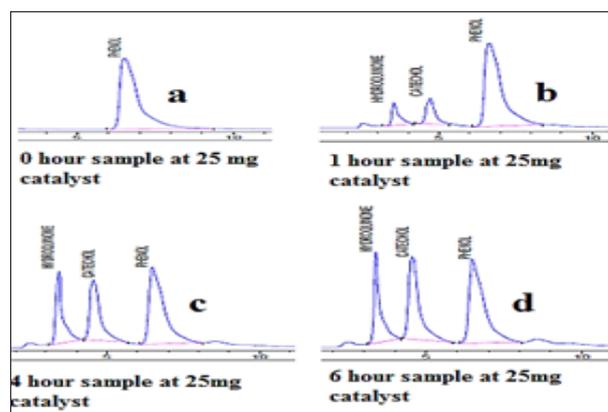


Fig 6 HPLC of 25mg agriculture RHA waste biocatalyst CYZ used reaction at different time intervals

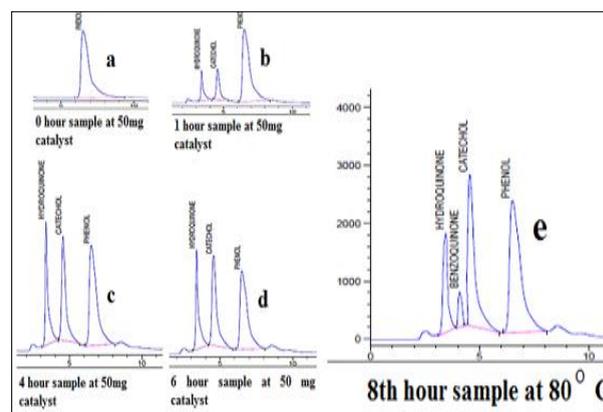


Fig 7 HPLC of 50 mg agriculture RHA waste biocatalyst CYZ used reaction at different time intervals

The resultant reaction outcomes have shown in (Table 1).

Table 1 Phenol hydroxylation HPLC outcomes at different conditions

Hour	Phenol area	Catechol area (mAU*Sec)	Hydro quinone area	Condition
0	104158.8	-	-	25 mg catalyst
1	96985.4	1154.9	11458.1	
4	92854.6	40514.9	31045.7	
6	88659.9	45874.8	34875.9	
0	105567.4	-	-	50 mg catalyst
1	94511.2	17842.7	12799	
4	83674.4	49981.5	38116.6	
6	81617.4	60674.7	39475.6	
0	106225.9	-	-	6 h and 50 mg catalyst
1	94867.4	16925.7	12548.9	
4	84275.8	48584.4	38064.6	
6	81593.7	59475.9	38954.4	
0	105236.9	-	-	8 h and 50 mg catalyst
1	93726.4	17164.2	12659.4	
4	84215.9	48954.9	37854.2	
6	81675.4	59254.7	38778.5	
8	80959.8	60224.2	38659.4	

From the chromatogram and peak the integrated results, this work observed the decreasing concentration of phenol and the increasing concentrations of the products such as Catechol and Hydro-quinone. Also, the product formation was calculated based on the peak area. 25 mg with 6 hours-maintained reaction yielded 25 percent of Catechol and Hydroquinone. But, 6 hours maintained 50 mg used hydroxylation reaction converted 75 percent phenol to 50% of Catechol and 25 percent Hydroquinone. Similarly, 50mg catalyst used 6 hours maintained 50 mg used hydroxylation reaction converted 75 percent phenol to 50

percent of Catechol and 25 percent Hydroquinone. The prolonged time up to 8 hours was not change yield. Hence, this work derived NaYZ and CYZ in acetic acid solvent and CYZ used as heterogeneous catalyst. Also, this work optimized the agriculture biocatalyst efficiency using HPLC. Second largest producer of rice is India which has produced approximately 104.41 -150 million tons of rice and 20 % of rice husk waste [29]. So, the part amount of the rice husk wastes can be converted to sodium silicate and copper silicate for adsorbent, heterogeneous catalytic active purposes respectively.

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