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AGRO-WASTE ORIGINATED HETEROGENEOUS SOLID ACID CATALYSTS TO ACCESS BIOACTIVE OXYGEN HETEROCYCLES

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ABSTRACT: Rice Husk Ash, an agro-waste by-product received renewed interest and represents an environmental issue in the social sphere. As a source of amorphous silica, the rice husk ash can be converted into valuable advanced materials. We have designed the solid acid catalyst embedding sulphonic group functionalities on rice husk ash and evaluated its catalytic efficiency for the synthesis of oxygen heterocycle such as 1,8-dioxo-octahydroxanthenes. The process is truly sustainable due to its operational simplicity, high conversion rate, and facile reusability of catalyst. The impact of this research can be remarkable in the valorization of amorphous silica from bioresource agro-waste for the synthesis of medicinally acclaimed industrial products.

Keywords: Amorphous silica, Rice Husk Ash, Xanthene, Sustainability.

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1.INTRODUCTION

Nowadays, a major problem before mankind is the production of excess waste from the agricultural sector. To maintain the ecological balance of our planet, utilizing these agricultural wastes in the main stream production is only one way to eradicate these problems [1]. The chemists are severely engaged in finding the sustainable solutions to human activities, especially related to the agricultural sector [2]. The researchers are trying to reduce the burden of agricultural waste on mother earth to a certain extent to raise awareness for a healthier planet [3]. Rice husk is a well-known, abundantly accessible agricultural waste obtained from rice milling industries across the world. When rice husk burns in an open atmosphere, the outer layer mound produces carbonized ash usually called Black Rice Husk Ash (BRHA). This carbonized ash, when subject to higher temperatures undergoes oxidation to form White Rice Husk Ash (WRHA), which predominantly serves as a potential source of amorphous silica [4-6]. Our potential research interest in rice husk ash is to utilize this natural source of silica in the valorized material. The silica obtained from rice husk ash consists of a highly porous structure with high specific surface area which provides an exceptional opportunity to use as a support material in designing solid acid catalyst [7-8]. In this context, we investigate the compatibility of rice husk ash as a support material in designing an eco-friendly catalyst and its utilization in the production of medicinally important heterocyclic compounds. Xanthenes are oxygen containing heterocyclic compounds characterized by the presence of biologically active 4H-pyran scaffolds in its framework. The presence of varied substituents at 9-position, xanthene skeleton exhibits a high impact on their applications in diverse fields such as anti-bacterial [9], anti-cancer [10], material science [11], dyes [12], anti-proliferative [13], anti-viral [14], antioxidant [15], etc. In the light of the aforementioned discussion and our research carried out on the development of solid acid catalyst as well as synthesis of biologically pertinent heterocyclic scaffolds [16-20], we herein report the synthesis of 1,8-dioxo-octahydroxanthenes using sulphonated rice husk ash.

2. MATERIALS AND METHODS

Experimental:

i) General Remarks:

Aryl aldehydes, chlorosulphonic acid and dimedone of best quality (AR Grade) were received as it is and used without further purification. The open capillary method is used for the determination of melting points of the synthesized products and are uncorrected. The chemical shifts (δ) are expressed in ppm. ^{1}H, ^{13}C and Fourier Transform Infra-Red spectra were measured on Bruker AC NMR spectrometer and Perkin-Elmer FT-IR spectrophotometer respectively. The progress of the reaction was monitored by TLC plates over silica gel-coated 60 F254 aluminum foil.

ii) Preparation of sulphonated rice husk ash:

The catalyst was prepared by using the literature procedure [21] as depicted in **Fig. 1**. FT-IR (cm^{-1}): 3327, 1157, 1105, 1025, 896, 831, 761, 663, 625, 595; SO_3H Loading: 0.121 mmol/g of RHA.

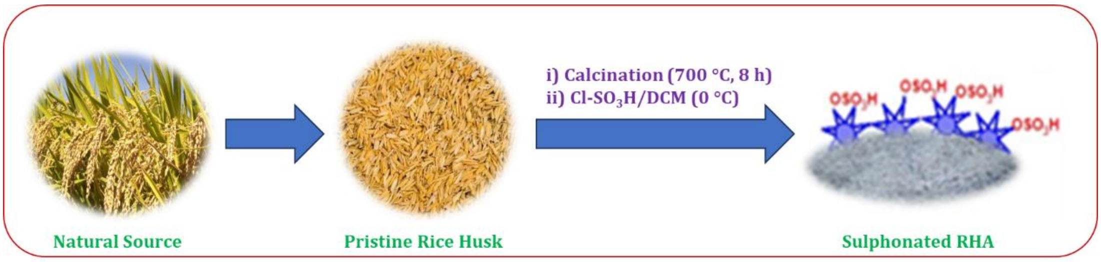


Fig. 1: Method of preparation for sulphonated rice husk ash.

iii) General procedure for synthesis of 1, 8-dioxo-octahydroxanthenes:

In a 25 mL round bottom flask, sulphonated rice husk ash (0.05 g, 0.006 mmol) was added to the aryl aldehyde (1 mmol) and dimedone (2 mmol) in ethanol (5 mL). The corresponding mixture was refluxed as time suggested in Table 2. The progress of reaction was continuously monitored by the TLC. Upon completion of the reaction, hot ethanol is added to the reaction mixture and filtered to remove the catalyst. Further, the solvent was evaporated, and recrystallization of the crude product from ethanol to generate anticipated 1,8-dioxo-octahydroxanthenes. The catalyst was separated from the reaction mixture by simple filtration, washed, dried, and used for the next cycle. The reusability of the catalyst was studied up to three cycles without notable reduction in the reaction yield of the expected product.

Spectral data of synthesised products:

3,3,6,6-Tetramethyl-9-(phenyl)-1,8-dioxo-octahydroxanthene (3a):

FT-IR (cm^{-1}): 3055, 2954, 2876, 1648, 1639, 1023, 957, 835, 679, 536; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.22-7.57 (m, 5H, Ar-H), 4.71 (s, 1H, CH), 2.16-2.29 (m, 8H, CH_2), 1.13 (s, 6H, CH_3), 0.99 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 27.6, 29.8, 33.5, 34.7, 51., 113.6, 126.8, 138.3, 156.4, 168.9, 193.8; MS (EI): *m/z* 350 $[M]^+$.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (3b):

FT-IR (cm^{-1}): 3021, 2927, 1688, 1646, 1372, 1190, 1023, 897, 755, 629, 511; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09-8.11 (t, *J* = 8.0 *Hz*, 2H), 7.47-7.48 (d, 2H), 4.80 (s, 1H, CH), 2.48 (s, 4H, CH_2), 2.15-2.25 (m, 4H, CH_2), 1.11 (s, 6H, CH_3), 0.98 (s, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 27.1, 29.5, 32.6, 40.5, 50.2, 114.5, 123.4, 129.3, 146.5, 151.5, 162.9, 196.2; MS (EI): *m/z* 395 $[M]^+$.

3,3,6,6-tetramethyl-9-(4-chlorophenyl)- 1,8-dioxo-octahydroxanthene (3c):

FT-IR (cm^{-1}): 3036, 2954, 1646, 1617, 1361, 1028, 946, 856, 706, 684, 593; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm): 7.42 (d, *J* = 9 Hz, 2H, Ar-H), 7.37 (d, *J* = 9 Hz, 2H, Ar-H), 4.89 (s, 1H, CH), 2.17-2.31 (m, 8H, CH_2), 1.15 (s, 6H, CH_3), 0.97 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 26.2, 30.3, 33.7, 34.1, 41.6, 51.9, 127.0, 130.3, 132.8, 144.7, 150.5, 196.2; MS (EI): *m/z* 384 $[M]^+$.

3,3,6,6-Tetramethyl-9-(4-cyanophenyl)-1,8-dioxo-octahydroxanthene (3e):

FT-IR (cm^{-1}): 3045, 2915, 2249, 1648, 1621, 1308, 1215, 1134, 992, 864, 768, 634, 525, 512; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50-7.54 (m, 2H, Ar-H), 7.22-7.29 (m, 2H, Ar-H), 4.77 (s, 1H, CH), 2.42-2.51 (m, 4H, CH_2), 2.11-2.20 (m, 4H, CH_2), 1.12 (s, 6H, CH_3), 0.98 (s, 6H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$): δ(ppm) 25.4, 29.6, 32.2, 41.8, 50.8, 110.4, 113.2, 117.0, 129.7, 132.9, 149.9, 162.1, 196.1; MS(EI): *m/z* 375 $[M]^+$.

3,3,6,6-Tetramethyl-9-(4-methylphenyl)- 1,8-dioxo-octahydroxanthene (3f):

FT-IR (cm^{-1}): 3067, 2945, 2878, 1622, 16508, 1334, 1060, 930, 836, 729, 636, 512; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm): 7.10-7.11 (d, *J* = 9 Hz, 2H, Ar-H), 6.98-6.99 (d, *J* = 9 Hz, 2H, Ar-H), 4.95

(s, 1H, CH), 2.32 (s, 3H, CH_3), 2.22-2.34 (m, 8H, CH_2), 1.17 (s, 6H, CH_3), 1.12 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 20.9, 27.4, 29.8, 31.3, 32.5, 47.2, 117.7, 128.9, 129.3, 135.5, 164.7, 190.6; MS(EI): *m/z* 364 $[M]^+$.

3. RESULTS AND DISCUSSION

The FT-IR spectrum (**Fig. 2**) of the catalyst displayed a peak at 3327 cm^{-1} belongs to OH stretching of SO_3H, and peaks at 1157, 1025 cm^{-1} show asymmetric and symmetric stretching of SO_2 group. The peak obtained at 896 cm^{-1} is for S-OH bending, while 663 cm^{-1} belongs to S-O symmetric stretching, indicating the successful grafting of the sulphonic group in the matrix of RHA. According to the literature [21], the below FT-IR data is in full agreement with the catalyst.

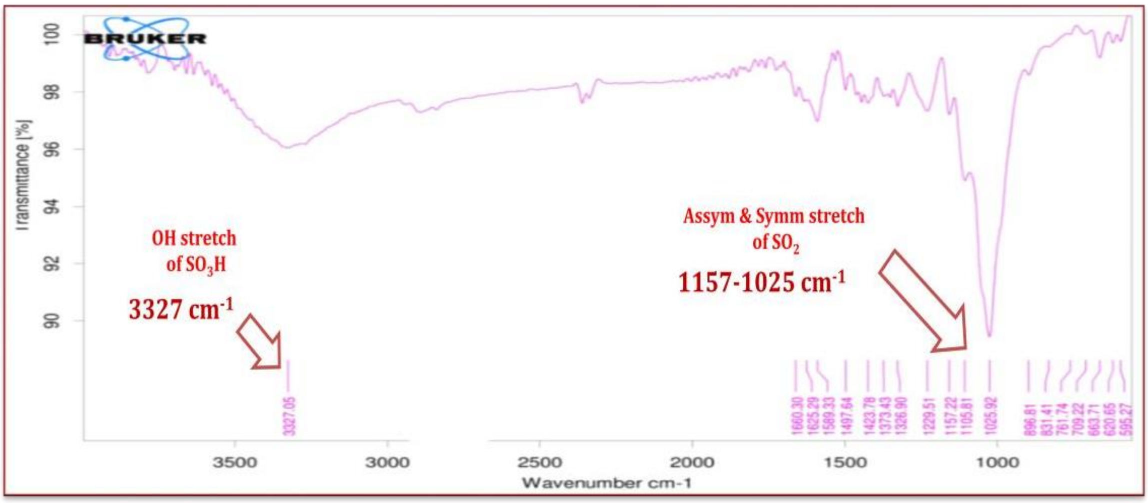


Fig. 2: FT-IR spectrum of sulphonated RHA.

In the beginning, we investigated the optimization of reaction conditions using the prepared catalyst. In this context, the reaction between p-nitro benzaldehyde (1 mmol) and dimedone (2 mmol) in the presence of a catalyst (0.05 g) was considered as a model substrate. The above model reaction is used for investigating the effectiveness of different solvents at reflux conditions (Table 1). The catalyst displayed a slow reaction rate in various solvents such as toluene, chloroform, diethyl ether, THF, and DMF to afford the corresponding 1,8-dioxo-octahyroxanthene in lower yields (Table 1, entries 1-5). Surprisingly, a high yield is obtained in the presence of ethanol as solvent under reflux condition (Table 1, entry 8). Furthermore, model reaction was investigated for the optimization of catalyst loading using varied quantities of catalyst. It was observed that the yield of the given product was enhanced significantly by increasing the quantity of catalyst, and an excellent yield was achieved for 0.05 g of catalyst (Table 1, entries 6-8). Further increase in catalyst quantity, no profound influence is observed on the yield of the anticipated product (Table 1, entries 9-10).

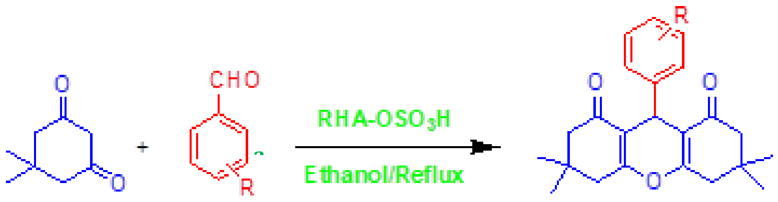
Table 1: Optimization of reaction condition and catalytic amount for given model reaction.

Entry	Catalyst Quantity (g)	Solvent/Temp.	Reaction Time (min)	Yield (%)
1	0.05	Toluene/Reflux	45	30
2	0.05	Chloroform/Reflux	45	32
3	0.05	Diethyl ether/Reflux	45	34
4	0.05	THF/Reflux	45	51
5	0.05	DMF/Reflux	45	64
6	0.01	Ethanol/Reflux	45	72
7	0.03	Ethanol/Reflux	45	84
8	**0.05**	**Ethanol/Reflux**	**45**	**92**
9	0.07	Ethanol/Reflux	45	92
10	0.09	Ethanol/Reflux	45	92

Reaction condition: Dimedone (2 mmol), p-nitrobenzaldehyde (1 mmol) and sulphonated RHA in solvent (5 mL) at given condition.

After the optimization of the reaction condition, we turned our attention towards evaluating the scope of protocol and efficiency of the catalyst. In this context, dimedone (1) reacted with a broad range of structurally diverse aromatic aldehydes (2) in the presence of sulphonated RHA (0.05 g) in a one-pot method to furnish the expected cyclization product of 1,8-dioxo-octahydroxanthenes. The results of this investigation are illustrated in Table 2. It can be seen that all reactions were catalyzes efficiently within 35 to 60 min to afford corresponding 1,8-dioxo-octahydroxanthenes in good to excellent yields. Aryl aldehydes including electron-withdrawing and donating functionality participated successfully in condensation reaction under the optimized reaction conditions (Table 2, entries 2-9). Furthermore, 2-nitrobenzaldehyde, 3,4,5-trimethoxybenzaldehyde and heteroaromatic furan-2-carboxaladehyde were also tolerated efficiently, providing good to moderate yield of the desired 1,8-dioxo-octahydroxanthenes (Table 2, entries 10-12).

Table 2: Sulphonated RHA catalyzed reaction between aldehydes and 1,3-dicarbonyl compound.

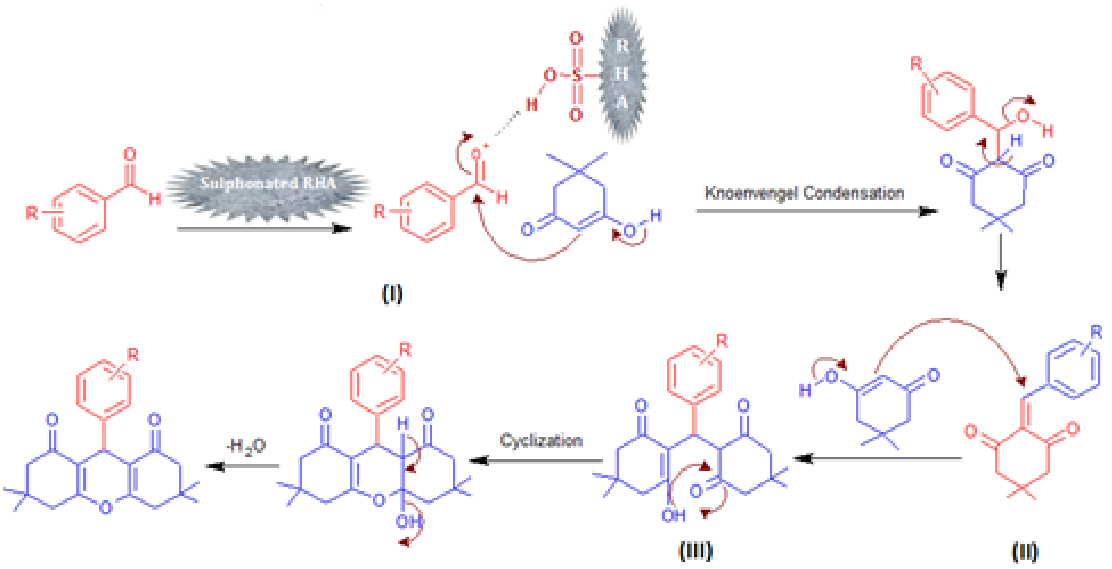


3a – 3l

Entries	Aryl Aldehydes (2)	Product (3)	Time (min)	Yield (%)^a	Mp (°C) [lit.]	Ref.
1	Benzaldehyde	**3a**	55	90	201-202 [201-203]	22
2	4-Nitrobenzaldehyde	**3b**	45	92	227-230 [228-230]	22
3	4-Chlorobenzaldehyde	**3c**	45	86	231-233 [230-232]	22
4	4-Bromobenzaldehyde	**3d**	55	85	238-240 [240-242]	22
5	4-Cyanobenzaldehyde	**3e**	35	91	219-222 [217-218]	22
6	4-Methylbenzaldehyde	**3f**	50	85	218-220 [219-221]	22
7	4-Hydroxybenzaldehyde	**3g**	55	86	250-252 [249]	23
8	3-Methoxybenzaldehyde	**3h**	55	80	175-176 [176-177]	24
9	4-Methoxybenzaldehyde	**3i**	50	84	247-249 [248-250]	25
10	2-Nitrobenzaldehyde	**3j**	45	85	249-251 [249-250]	25
11	3,4,5-Trimethoxybenzaldehyde	**3k**	55	81	207-208 [206-208]	19
12	Furfural	**3l**	60	80	64-65 [63-65]	26

Reaction condition: Dimedone (2 mmol), aryl aldehyde (1 mmol), and sulphonated RHA in ethanol (5 mL) were stirred at reflux condition. ^{a} Isolated yield.

A suggested mechanistic pathway for the synthesis of xanthene derivatives has been discussed in Scheme 1. Our potential solid acid catalyst synergistically behaves as an efficient host which readily activates the aldehyde (I) and underwent nucleophilic attack with keto-enol form of a first mole of 1,3-dicarbonyl compound to obtain the intermediate (II). Michael addition occurs between intermediate (II) and second mole of 1,3-dicarbonyl compound to furnish the intermediate (III). Lastly, cyclization and water removal from (III) produce the expected xanthene derivatives.



Scheme 1: Suggested mechanism for the formation of xanthene derivatives.

The catalytic efficiency of sulphonated RHA has been compared with other reported catalysts for the synthesis of 3b (synthesized xanthene derivatives), and the results are illustrated in Table 3. Based on the comparisons presented above, the aforementioned catalyst displayed high catalytic efficiency in the yield of synthesized product and also required less time for completion of the reaction as compared to reported protocols.

Table 3: Catalytic efficacy of sulphonated RHA with other protocols.

Entry	Catalyst used	Reaction condition	Time (Min)	Yield (%)	Ref.
1	Sulphonated RHA (0.05 g)	Ethanol/Reflux	45	92	This Work
2	CAN/HY-zeolite	Solvent-free/80°C	90	88	27
3	PEG-SO_3H (20 mol %)	Solvent-free/80°C	95	86	28
4	Fe_2O_3 nanoparticles	Ethanol/RT	135	90	29
5	$CaCl_2$ (20 mol %)	DMSO/90°C	240	85	30
6	L-Proline (40 mol %)	Dichloroethane/Reflux	360	83	31
7	β-Cyclodextrin	Water/65°C	600	96	32

4. CONCLUSION

In this framework, we describe the valorization of amorphous silica obtained from rice husk ash, an underutilized waste of the rice milling industry, in combination with chlorosulphonic acid in the preparation of the catalyst, sulphonated rice husk ash. The catalytic efficiency of the aforesaid catalyst is found to be highly competent in the one-pot synthesis of medicinally important xanthenes. Operational simplicity, cleaner reaction profile, high yields, short reaction time, and facile reusability of catalyst are the alluring features of the present protocol.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals or humans were used for the studies that are based on this research.

CONSENT FOR PUBLICATION

Not applicable.

FUNDING

None.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interests.

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