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ZrBDC MOF AS A SUSTAINABLE CATALYST FOR EFFICIENT HYDROLYSIS OF LIGNOCELLULOSIC BIOMASS

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ABSTRACT. In this study, ZrBDC MOF was synthesized sustainably using water as the sole green solvent, at room temperature, and without modulation. The as-synthesized ZrBDC MOF exhibited a semi-crystalline structure with desirable properties such as a specific surface area of 435.37 m^2/g and a pore volume of 0.51 cm^3/g. The evaluation of this MOF as a solid-acid catalyst for the hydrolysis of lignocellulosic biomasses, especially sugarcane bagasse and pineapple peels was conducted for the first time in this study. Alkaline hydrogen peroxide pretreatment increased cellulose contents to 79.12 ± 0.69% in SCB and 81.49 ± 1.49% in PP. Under optimum conditions, a mixture of 4.0 g biomass (sugarcane bagasse or pineapple peels) and 0.8 g of ZrBDC MOF in 100 mL distilled water was hydrolyzed at 130 °C for 4 h. The hydrolysis process yielded 0.60 mg/mL and 2.044 mg/mL of total reducing sugar (TRS), mainly glucose, from the hydrolysis of sugarcane bagasse and pineapple peels, respectively. These promising results demonstrated the potential of ZrBDC MOF as an alternative catalyst for the hydrolysis of lignocellulosic biomass, enabling the conversion of cellulose to glucose for bioethanol production. The use of ZrBDC MOF offers economic feasibility and environmental friendliness, addressing the challenges associated with homogeneous acid hydrolysis.

KEY WORDS: Metal organic frameworks (MOFs), Catalyst, Lignocellulosic biomass, Hydrolysis, Total reducing sugar (TRS), Bioethanol

INTRODUCTION

The utilization of biomass as a renewable substitute for fossil feedstocks in the production of chemicals and fuels is growing [1, 2]. Lignocellulosic biomass is the most abundant feedstock for the production of bioethanol. Agricultural residues, the organic portion of municipal solid wastes, forest biomass and wastes, and energy crops are the primary sources of lignocellulose [3-5]. Using lignocellulosic biomass for fuel has numerous benefits, such as lower environmental impact, financial gains, resolution of the fuel vs. food debate, and a desirable substitute for disposing of these residues. Lignocellulosic bioethanol can be obtained by two distinct steps: hydrolysis and fermentation, by running each step under its optimum operating conditions. Enzymatic hydrolysis of pretreated biomass can be achieved using cellulase, although the reaction may be constrained by activity loss, reaction conditions, and product inhibition [6-8].

Catalysis is an environmentally friendly and economically appealing technology that can meet customer demands for ever-higher-quality goods and services while still being environmentally conscious [9]. Metal-Organic Frameworks (MOFs) are a newly developed family of porous materials characterized by a high specific surface area, well-organized configuration, and ordered and tunable pore structures [10-15]. It is anticipated that MOFs' remarkable characteristics will result in remarkable catalytic performances.

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ZrBDC works well at a very small scale using a joint effort of things like structural defects (missing BDC linkers or Zr^{4+} nodes within its framework), active acidic centers, and confinement effects within its porous network. This exposes zirconium ions (Zr^{4+} sites) on the $Zr_6O_4(OH)_4$ metal nodes, which act as strong Lewis acid sites, while the surface of ZrBDC also has -OH groups, which serve as Brønsted acid sites. The water molecules attach to the unsaturated Zr-sites and become polarized, creating nucleophilic hydroxide ions and acidic protons. These active species then attack the oxygen atoms of glycosidic bonds that hold the sugar monomers together in cellulose or hemicellulose chains. This stretches the glycosidic bond, making it easier for water to break it down into sugars like glucose. This structural synergy allows ZrBDC is a good candidate to break down biomass efficiently [16].

The applications of MOFs as heterogeneous catalysts for the hydrolysis of biomass (cellulose) have been reported by very few researchers. For example, Akiyama *et al.* [17] tested the catalytic activity of the MIL-101Cr-SO_3 MOF in cellulose hydrolysis and obtained a very poor yield of 1.4% glucose. Here, a large amount of MIL "catalyst" relative to the substrate used (200 mg catalyst vs. 25 mg cellulose) makes the process economically not feasible. Besides, the catalyst was synthesized at a high temperature (180 ºC) that takes a long period of time (6 days) using a hazardous solvent such as DMF. Additionally, Ahmed *et al.* [7] also evaluated the catalytic potential of the UiO-66 MOF, which was synthesized using a hazardous DMF solvent for the hydrolysis of carboxymethyl cellulose (CMC) at 120 ºC for 1 h. However, the contribution of the MOF in the hydrolysis of polymeric CMC was insignificant at the studied temperature. This indicates that there is a gap in synthesizing MOFs in a greener way and applying them as heterogeneous catalysts for the hydrolysis of real lignocellulosic biomasses. Therefore, in this work, we have synthesized a ZrBDC MOF at room temperature by using water as the sole solvent and evaluated its catalytic potential for the hydrolysis of real lignocellulosic biomasses (sugarcane bagasse and pineapple peels) for the first time.

MATERIALS AND METHODS

Materials

Analytical grade chemicals such as zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$, 98%, Sigma Aldrich, USA), terephthalic acid (H_2BDC, 98%, Sigma Aldrich, USA), sodium hydroxide pellets (NaOH, Rankem Laboratory Reagent, India), ethanol (C_2H_5OH, absolute, Carlo Erba Reagents, France), sulfuric acid (H_2SO_4, 98%, Carlo Erba Reagents, France), 3,5-dinitrosalicylic acid (DNS, Abron Chemicals, India), sodium potassium tartrate ($C_4H_4O_6KNa.4H_2O$, T.Gerrard & Co.Ltd. Biological Laboratories, UK), hydrogen peroxide (H_2O_2, 30%, Dallul Pharmaceuticals, Ethiopia), acetone (UNI-CHEM chemical reagents, UK), and D-glucose (GuangZhou Jinhuada chemical Reagent Co.Ltd., China) were used.

Lignocellulosic biomasses such as sugarcane bagasse (SCB) and pineapple peels (PP) were also used. Moreover, apparatuses/instruments such as a drying oven (GX-65B, China), hot plate (MSH-300i, England), UV-vis spectrophotometer (Jeneway 6850, UK), pH meter (Jenway 3510, UK), shaker (Model no. SHO-2D, Korea), autoclave (DIXONS Surgical Instruments Ltd, UK), centrifuge (Model no. 80-2A), electronic balance (Model no. JD210-4, UK), muffle furnace (SX-2.5/10, China), desiccator, water bath, filtering crucibles, erlenmeyer flasks, filter paper, a sieve of mesh size 0.5 mm (Model no.SSIC-90, SISCO, India), and grinder (Model no. GCG684, Geepas, UAE) were used in this study.

Sample collection and preparation

Two lignocellulosic biomasses sugarcane bagasse (SCB) and pineapple peels (PP) were collected from juice houses found in Addis Ababa city, Ethiopia. The collected samples were air-dried, then chopped, ground, and milled using a grinder, and sieved through a 0.5 mm mesh (Figure 1). 1.5 Kg of each of the SCB and PP powder were measured and kept inside different vessels.

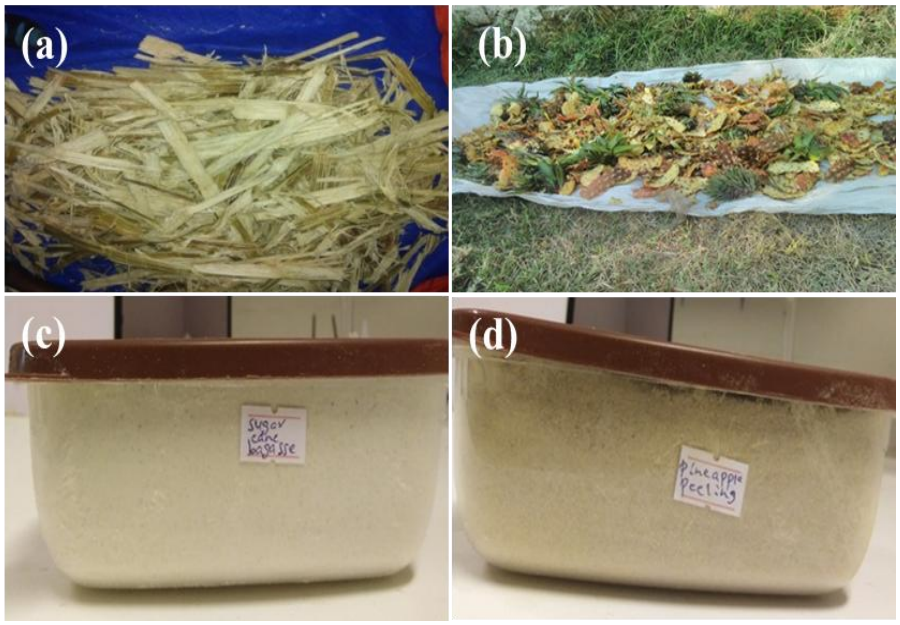

Figure 1. Sample preparation processes: sugarcane bagasse (a), pineapple peels (b), sugarcane bagasse powder (c), and pineapple peels powder (d).

Composition analysis of the raw and pretreated SCB and PP

The composition of the raw and pretreated biomass (SCB, PP) material was determined using the gravimetric method mentioned elsewhere [18].

Extractives: Dried raw biomass (SCB, PP) weighing 2.5 g was loaded into a cellulose thimble. Moreover, 150 mL of acetone was used as a solvent for extraction and transferred into a round-bottom flask. Then, after the Soxhlet extractor was configured, residence times for the boiling and rising stages were carefully adjusted to 70 ºC and 25 min, respectively, on the heating mantle for 4 h. Following extraction, the sample was air-dried for a few minutes at room temperature. The extracted material was then dried in an oven at 105 ºC until a constant weight was achieved. The % (w/w) of the extractives content was calculated by dividing the weight of the extractives by the weight of the dried raw biomass and multiplying by 100 [19-21].

Hemicellulose: A dried extracted/pretreated biomass (1.0 g of SCB, PP) was weighed and transferred into a 250 mL Erlenmeyer flask. Then, 150 mL solution of 0.5 mol/L NaOH was added to the flask containing the biomass. The mixture was boiled for 3.5 h with distilled water. After boiling, the mixture was allowed to cool, filtered through vacuum filtration, and washed repeatedly with distilled water until it reached a neutral pH. The residue was dried in an oven at

105 ºC until it reached a constant weight. The hemicellulose content (%w/w) was calculated by dividing the weight of hemicellulose that was extracted during the process by the initial biomass weight and multiplying it by 100 [19-22].

Lignin: Dried extracted raw/pretreated biomass (300 mg of SCB, PP) was weighed and transferred into a glass test tube. Then, 3 mL of 72% H_2SO_4 was added to the biomass in the test tube. The sample was kept at room temperature for 2 h with careful shaking at 30 min intervals to ensure complete hydrolysis. After the initial hydrolysis, 84 mL of distilled water was added to the test tube to dilute the mixture. The diluted mixture was transferred to an autoclave and subjected to hydrolysis for 1 h at 121 ºC. After the hydrolysis in the autoclave, the slurry was cooled to room temperature. The hydrolysates were separated from the solid residue by vacuum filtration using a filtering crucible. The residues remaining on the filtering crucible were washed with distilled water. Then, they were transferred to weighing filters and dried in an oven at 105 ºC until constant mass was achieved. The dried residues were incinerated at 575 ºC in a muffle furnace to determine the ash content. The percentage of insoluble lignin was calculated relative to the dry sample mass using Equation 1. The acid soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320 nm. The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin [23].

$$\%L_{Ki} = \frac{M_k - M_c}{M_A} \text{x } 100 \quad (1)$$

Where L_{Ki} is Lignin Klason insoluble; M_k is the mass of dry insoluble lignin; Mc is the ash mass of the insoluble lignin; M_A is the dry sample mass.

Ash: To determine the total ash, 1.0 g of dried extracted raw/pretreated biomass (SCB, PP) was weighed and transferred into a previously weighed porcelain crucible. The sample was then incinerated at 575 ºC in a muffle furnace for 2 h. The ash content was determined by mass difference using Equation 2.

$$\% \text{ ash} = \frac{M_c}{M_a} \text{x } 100 \quad (2)$$

Where % ash is the percentage by mass of ash; M_c is ash mass (the difference between the mass of the crucible with ash and the mass of the empty crucible); M_a is mass of the dried raw biomass sample.

Cellulose: The cellulose content (%w/w) was determined by difference, assuming that cellulose, hemicellulose, lignin, extractives, and ash are the only components present in the lignocellulosic biomass [19-21].

Pretreatment of SCB and PP

In this study, SCB and PP were pretreated by the alkaline hydrogen peroxide pretreatment method previously used by Rabelo et al.[24]. The pretreatment was performed under optimal conditions of 7.35% (w/v) peroxide at 25 ºC for 1 h. In brief, the pretreatment solution of alkaline peroxide was prepared by adding 24.5 mL of 30% H_2O_2 to 75.5 mL of distilled water, and the pH was adjusted to 11.5 with sodium hydroxide.

In each pretreatment run, 4.0 g of each biomass sample (SCB, PP) was treated at 25 ºC for 1 h with 100 mL of 7.35% hydrogen peroxide in 500 mL flasks by stirring at 150 rpm. Following the pretreatment step, the liquors were separated from the solid fraction by filtration. The solids fraction was washed many times to remove the water-soluble solids, dried at room temperature, and its mass was weighed to determine the pretreatment yield and chemical composition [23,25]. Then, 1 M H_2SO_4 was added to the pretreatment liquor obtained above to a pH of 2 to precipitate

lignin. After the precipitated lignin was washed with distilled water and dried at room temperature, its mass was weighed.

Synthesis of ZrBDC MOF

The methodology previously used by Yassin *et al.* [26, 27] was followed in the synthesis of ZrBDC MOF with some modifications. In brief, 1.95 g (6.05 mmol) of $ZrOCl_2.8H_2O$ was dissolved in 28 mL of distilled water (solution 1), and in separate beakers, 1.03 g (5.655 mmol) of H_2BDC was suspended in 22 mL of distilled water. Subsequently, 13 mL of 1.0 M NaOH solution was gradually added to the linker suspension as a deprotonating agent, and the resultant mixture was then stirred for 30 min until reaching a clear solution (solution 2). Next, solution 1 was transferred dropwise into solution 2 or vice versa, resulting in an instantaneous precipitate of a white solid. The sample was left under stirring at 300 rpm with a magnetic stirrer for 24 h at room temperature. The formed solid was centrifuged and washed with 50 mL of distilled water (three times) and with 35 mL of ethanol (two times). The sample was then dried at 80 ^oC in an oven. Finally,1.4 g of a white solid ZrBDC was obtained.

Characterization of the ZrBDC MOF

The synthesized ZrBDC MOF was characterized using various advanced techniques. To determine the crystalline structure and phase purity of the as-synthesized material, Powder X-ray Diffraction (PXRD) patterns were recorded using a Philips X'PERT diffractometer equipped with an X'Celerator detector and employing Cu Kα radiation with a wavelength of 1.5418 Å. The diffraction patterns were registered in the 2θ range from 4 to 90^o. N_2 sorption properties were measured at -196 ^oC (77 K) using a Micromeritics instrument ASAP 2420 device. Approximately 100 mg of each sample was prepared and subjected to outgassing at 150 ^oC under high vacuum for 16 h before the measurements of any isotherms. The Brunauer-Emmett-Teller (BET) method was used to estimate the surface area of the material. The t-plot approach was used to determine the material's micropore and external surface areas. The total pore volume and average pore radius were estimated from the relative pressure close to unity (p/p_o = 0.98). The morphology of the ZrBDC MOF was examined using a high-resolution Philips XL 30 SEM device.

Hydrolysis of the pretreated SCB and PP using ZrBDC MOF

The hydrolysis was carried out on the pretreated lignocellulosic biomass (SCB, PP) by optimizing the amount of ZrBDC MOF, biomass loading (SCB, PP), temperature and hydrolysis time using the one factor at a time method [28], that is, adjusting one variable at a time while maintaining the same value for the others. The following is an outline of the process for each parameter.

Optimization of ZrBDC MOF Mass

About 4.0 g of each pretreated biomass (SCB, PP) was taken and placed in a round bottom flask. Then, different amounts of the ZrBDC MOF catalyst (0.4, 0.6, 0.8, 1.0, and 1.2 g) were added to each biomass sample. Finally, 100 mL of distilled water was added to each sample in a round-bottom flask. The flask containing the mixture was fitted with a condenser to prevent solvent loss through evaporation and placed on a hot plate with a magnetic stirrer. Then, the mixture was heated at 130 ^oC for 4 h independently with continuous stirring at 300 rpm. A control sample reaction without the ZrBDC MOF catalyst was also carried out under the same conditions. At the end of the reaction, each flask was removed from the hot plate and rapidly cooled to room temperature. The mixture was then centrifuged at 2058 x g for 5 min to separate the solids. The

clear hydrolysate obtained after centrifugation was used for the determination of total reducing sugars.

The total reducing sugar (TRS) of the hydrolysate was determined by the dinitrosalicylic acid (DNS) method. Thus, 1 mL of the clear hydrolysate was placed into a 25 mL test tube, and then 3 mL of dinitrosalicylic acid (DNS) reagent was added to the test tube. The reaction mixture was heated in boiling water for 5 min, resulting in the development of a red color, indicating the presence of reducing sugars. After cooling the mixture, the absorbance was measured using a UV-vis spectrophotometer at a wavelength of 540 nm. The TRS concentration was calculated by employing a standard calibration curve prepared using a glucose solution [29, 30]. The TRS concentration was calculated using Equation 3:

$$\text{TRS concentration} = \frac{(\text{absorbance of the hydrolysate}) - (\text{y-intercept})}{\text{slope}} \quad (3)$$

Optimization of biomass (SCB, PP) load

About 3.0, 3.5, 4.0, 4.5, and 5.0 g of each pretreated biomass (SCB, PP) were taken along with the optimized ZrBDC MOF catalyst concentration and placed in a round-bottom flask. Then, 100 mL of distilled water was added to each sample in a round-bottom flask. The mixture was heated at 130 ºC for 4 h independently with continuous stirring at 300 rpm. The hydrolysis procedure and TRS determination were carried out in the same way as described previously for the ZrBDC MOF catalyst concentration.

Optimization of hydrolysis time

The hydrolysis time was optimized by varying the time from 1 to 5 h while keeping the biomass loading and ZrBDC MOF catalyst amount at the optimized values and the temperature at 130 ºC. The hydrolysis procedure and TRS determination were carried out in the same way as described previously for the ZrBDC MOF catalyst concentration.

Optimization of hydrolysis temperature

The hydrolysis of optimized biomass (SCB, PP) was performed in a round-bottom flask at different temperatures of 50, 90, and 130 ºC. The ZrBDC MOF catalyst concentration and hydrolysis time were kept at the previously optimized values. The hydrolysis procedure and TRS determination were carried out following the same steps as described for the ZrBDC MOF catalyst concentration. Finally, TRS (mg/mL) obtained during hydrolysis was taken into consideration to calculate the hydrolysis yield. It was calculated as follows [31]:

$$\text{Hydrolysis (\%)} = \frac{\text{TRS concentration obtained x total volume of hydrolysate}}{\text{mass of sample used}} \text{ x } 100 \quad (4)$$

RESULTS AND DISCUSSION

Chemical compositions of raw SCB and PP

The compositional analysis of the raw SCB and PP was determined using the gravimetric method. Biomass compositions can vary depending on whether they are classified as woody or non-woody biomass, the methods developed for analysis, the geographical locations of materials, differences in solvents used, biomass variety, and the different parts of plants used in the compositional analysis [18].

The compositions of the two lignocellulosic materials are shown in Table 1. Each experiment was done in triplicate; reported results indicate the average mean values of the triplicate

experiments. Therefore, the chemical composition of raw SCB was 48.36 ± 0.44% cellulose, 24.0 ± 0.46% hemicellulose, 20.66 ± 0.49% lignin, 4.19 ± 0.04% ash, and 2.37 ± 0.03% extractives. Moreover, the chemical composition of raw PP was 42.83 ± 0.39% cellulose, 21.37 ± 0.67% hemicellulose, 10.24 ± 0.24% lignin, 9.2 ± 0.26% ash, and 15.2 ± 0.4% extractives.

Table 1. Chemical composition of raw SCB and PP (% w/w).

Materials	Component (% w/w)				
	Cellulose	Hemicellulose	Total lignin	Ash	Extractives
SCB	48.36 ± 0.44	24.0 ± 0.46	20.66 ± 0.49	4.19 ± 0.04	2.37 ± 0.03
PP	42.83 ± 0.39	21.37 ± 0.67	10.24 ± 0.24	9.2 ± 0.26	15.2 ± 0.4

The results in this study are comparable to other reported values in the literature [28,32]. For example, Paturau *et al.* [33] reported 26-47% cellulose, 19-33% hemicellulose, 14-23% lignin, and 1-5% ash content for SCB. Moreover, Sherif *et al.* [28] reported 41.54 ± 2.31% cellulose, 21.97 ± 0.81% hemicellulose, 10.37 ± 0.46% lignin, 8.80 ± 0.04% ash, and 15.49 ± 0.13% extractives content for PP. The content of cellulose in SCB and PP were 48.36 ± 0.44% and 42.83 ± 0.39%, respectively, showing that SCB and PP were good substrates for fermentable sugar production.

Effect of alkaline hydrogen peroxide pretreatment on SCB and PP

Pretreatment is considered an essential step in a biorefinery to reduce the recalcitrance of biomass. In this study, pretreatment was performed using alkaline hydrogen peroxide (AHP). AHP treatment has been shown to have an oxidative action on the cell wall of biomass, resulting in the breaking of ester linkages within the cell wall matrix. This oxidative action promotes the disruption of lignin-carbohydrate complexes and the removal of lignin from the biomass, thereby increasing the digestibility of the biomass [34]. In the presence of NaOH, the intramolecular ester bonds between lignin and hemicellulose can undergo saponification, resulting in the extraction of lignin from the lignin-hemicellulose complex [35]. Thus, AHP pretreatment is used to achieve higher lignin removal during the biomass (SCB and PP) pretreatment process [34].

In this study, the white color of the raw SCB was changed to a light yellow color, while the dark brown color of the PP was changed to a light yellow color after the biomass was pretreated with AHP. The change in color of the raw SCB and PP after treatment with AHP indicates changes in chemical composition (Table 2), with the removal of non-cellulosic materials such as ash, extractives, hemicellulose, lignin, and oils. The content of cellulose increased to 79.12 ± 0.69 %, while hemicellulose (11.03 ± 0.25%), lignin (8.13 ± 0.21 %), and ash (1.46 ± 0.06%) decreased (Table 2) when SCB was pretreated with AHP. Similarly, the content of cellulose increased to 81.49 ± 1.49%, while hemicellulose (12.19 ± 0.35%), lignin (2.51 ± 0.03%), and ash (2.02 ± 0.02%) decreased (Table 2) as expected when PP was pretreated with AHP, indicating the effectiveness of AHP treatment in removing recalcitrant lignin and making cellulose more accessible to ZrBDC MOF for hydrolysis.

Table 2. Chemical composition of pretreated SCB and PP by AHP (% w/w).

Materials	Component (% w/w)			
	Cellulose	Hemicellulose	Total lignin	Ash
Pretreated SCB	79.12 ± 0.69	11.03 ± 0.25	8.13 ± 0.21	1.46 ± 0.06
Pretreated PP	81.49 ± 1.49	12.19 ± 0.35	2.51 ± 0.03	2.02 ± 0.02

Characteristics of the ZrBDC MOF

a) XRD pattern of ZrBDC MOF

Figure 2a shows the XRD pattern of the as-synthesized ZrBDC MOF prepared under sustainable conditions-water as a solvent and at room temperature, unlike the conventional approach which uses DMF as a solvent and relatively high temperature i.e. 120 ºC (even higher temperature was applied!!). The successful synthesis and phase purity of ZrBDC MOF crystals was confirmed by comparing the X-ray diffraction pattern of the synthesized MOF with elsewhere reported experimental plus theoretical data [26, 27]. All the important peaks of the ZrBDC MOF are observed at the corresponding 2 theta values when compared with the theoretical XRD pattern mentioned elsewhere [26, 27]. The major peak exhibited around 2 theta of 8.1º typically evidences the formation of ZrBDC MOF with the (111) plane. Although the peak shows in the range from 30 to 40 degrees, making this MOF similar to UiO-66, the peak apparent around 2 theta of 15o and 28.2o could be associated with the linker or residual terephthalic acid presence due to insufficient washing. The presence of such linkers could be justified by the relatively lower specific surface area of the as-synthesized MOF compared with a previous similar report by Yassin *et al.* [26]. It appears that the MOF has a semi-crystalline structure since broadened reflections are observed. Yassin *et al.* [26, 27] also reported that ZrBDC MOF has a semi-crystalline and a UiO-66 type MOF structure.

b) Textural Properties of ZrBDC MOF

The nitrogen adsorption-desorption isotherms at 77 K for ZrBDC MOF are depicted in Figure 2b. The material exhibited a significant uptake of nitrogen at lower relative pressure values ($P/P_o < 0.1$), which suggests the presence of micropores within the material and seems to be a Type II isotherm. Moreover, the BET results indicate that the ZrBDC MOF has a specific surface area of 435.37 m^2/g and a pore volume of 0.51 cm^3/g. The relatively lower specific surface area (435.37 m^2/g) compared with a similar MOF prepared by Yassin *et al.* [26, 27] (461 m^2/g) could be due to residual linker not removed by washing.

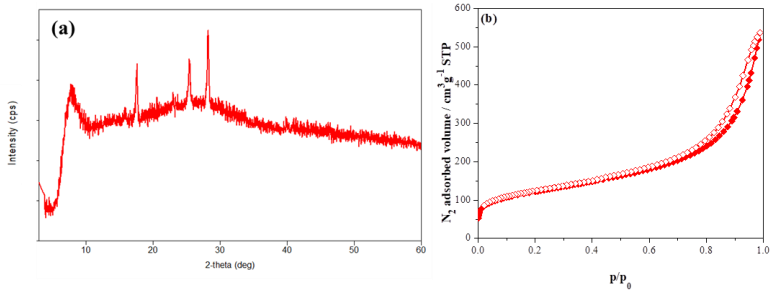

Figure 2. PXRD pattern of ZrBDC MOF (a) and Nitrogen adsorption-desorption isotherm for ZrBDC MOF (b).

c) Morphological properties of ZrBDC MOF

The SEM images of the ZrBDC MOF show different sized irregular-shaped particles (Figure 3a-c) and the EDS analysis confirms that there are no other impurity elements than the ZrBDC composition (Zr, C, and O) (Figure 3d).

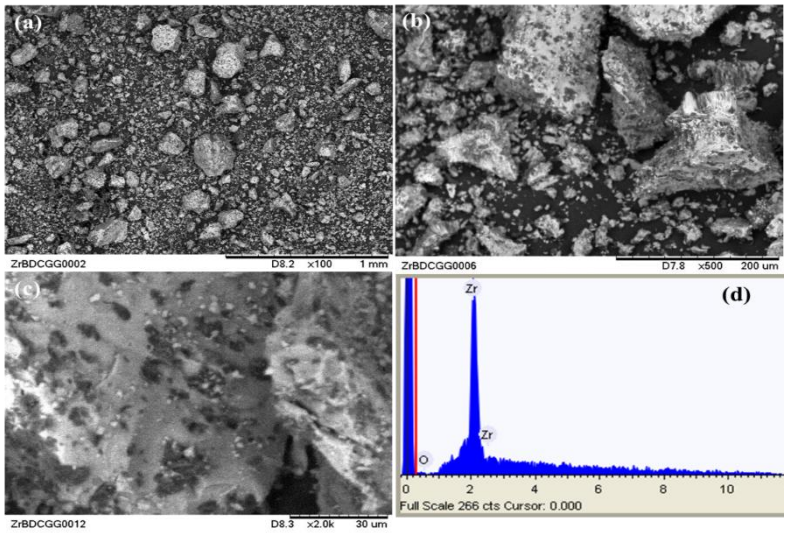

Figure 3. SEM images (a-c) and EDS spectra (d) of ZrBDC MOF.

Optimum parameters for the hydrolysis of pretreated SCB and PP

The hydrolysis of pretreated SCB and PP was optimized with respect to ZrBDC mass, SCB and PP loading, reaction temperature and time using a one factor at a time approach. In the literature, different researchers use different ranges of the parameters (temperature, time, and amount of catalyst) for the hydrolysis of biomass. For example, Sherif *et al.* [28] used temperature ranges of 90, 110, 130, and 150 °C in the time range of 1 to 4 h and catalyst concentrations of 0.05, 0.1, and 1 M for the hydrolysis of multisubstrate biomass. Besides, Ahmed *et al.* [7] used temperature ranges of 50, 80,100 and 120 °C for the hydrolysis of 50 mg of cellulose for 1 h. Additionally, Rekha *et al.* [36] have used 3.0 g biomass, 0.1 to 0.3 g of catalyst at temperature ranges of 30, 45, and 60 °C for 1 h for the hydrolysis of corncob. Thus, this indicates that different ranges of parameters were used in the literature. Therefore, in our study, we have used a ZrBDC MOF catalyst mass in the range of 0.4 to 1.2 g, a pretreated SCB and PP mass in the range of 3 to 5 g at a temperature range of 50, 90, and 130 °C in a time range of 1 to 5 h for optimizing the parameters for the hydrolysis of pretreated SCB and PP.

Optimum parameters for the hydrolysis of pretreated SCB

Hydrolysis of 4 g of pretreated SCB was carried out with varying amounts of ZrBDC MOF (0.4, 0.6, 0.8, 1 and 1.2 g) at 130 °C for 4 h to optimize the mass of the catalyst. Therefore, different MOF masses, i.e., 0.4, 0.6, 0.8, 1 and 1.2 g, resulted in a TRS yield of 0.56, 0.58, 0.60, 0.60 and 0.59 mg/mL, respectively (Figure 4a). An increase in mass of ZrBDC MOF from 0.4 to 0.8 g resulted in an increase in TRS yield (from 0.56 to 0.60 mg/mL), but slightly decreased beyond 1 g of ZrBDC MOF. The decrease in TRS content with further increase in ZrBDC MOF mass may be due to further decomposition of sugars into other by-products. Hence, 0.8 g of ZrBDC MOF provided the maximum TRS yield (0.60 mg/mL) and was employed for hydrolysis of pretreated SCB in subsequent optimization studies.

To get the optimum loading of SCB for hydrolysis, the reaction was carried out using the optimum amount of ZrBDC MOF (0.8 g) at 130 °C for 4 h with varying amounts (3, 3.5, 4, 4.5 and 5 g) of SCB. As depicted in Figure 4b, the maximum TRS yield of 0.60 mg/mL was obtained

at 4 g of SCB. A slight reduction in reducing sugar yield occurred beyond 4 g of SCB. The decrease in TRS content may be due to the decrease in the adsorption capacity of the ZrBDC MOF catalyst as a result of high substrate loading that slows down mass transfer phenomena. Thus, the results suggest that 4 g is the optimum amount of SCB for the hydrolysis reaction under the given reaction conditions.

Hydrolysis time is one of the most critical factors among different physical factors affecting the yield of sugar during the hydrolysis of lignocellulosic biomass. To optimize time, the hydrolysis was carried out using 4 g of SCB and 0.8 g of ZrBDC MOF at 130 ºC by varying time from 1 to 5 h. As shown in Figure 4c, there is a gradual increase in TRS yield from 0.244 to 0.289 mg/mL for the reaction period of 1 to 2 h. Besides, the reducing sugar yield increases linearly for the reaction period of 3 to 4 h, reaching a maximum TRS yield of 0.60 mg/mL at 4 h. Beyond 4 h, the TRS concentration is almost similar to the TRS concentration obtained at 4 h, but the volume of TRS hydrolysate decreases due to the loss of more water through evaporation. Hence, 4 h is found to be the optimum hydrolysis time, which led to the production of 0.60 mg/mL of TRS.

The reaction temperature is a critical criterion in hydrolysis processes and can significantly impact the sugar yield obtained from biomass. To study the effect of temperature on the hydrolysis process, experiments were conducted at three different temperatures: 50, 90, and 130 ºC by keeping ZrBDC MOF mass, SCB mass, and time at the optimum values. As shown in Figure 4d, the TRS yield at 50 and 90 ºC was very low (i.e., 0.053 and 0.056 mg/mL, respectively) when compared to the yield at 130 ºC, which is 0.60 mg/mL. This indicates that the catalytic effect of the ZrBDC MOF below 100 ºC was very low. Hence, the optimum temperature of the hydrolysis using the ZrBDC MOF catalyst under the given reaction conditions is 130 ℃, which gave 0.60 mg/mL of TRS. Moreover, we have tried the hydrolysis reaction beyond 130 ºC. However, the slurry solidified quickly during the hydrolysis due to significant water loss through evaporation before the reaction reached completion.

Therefore, by employing the optimum values (0.8 g of ZrBDC MOF, 4 g of SCB, 4 h, and 130 ºC) of the four parameters together, we have evaluated the catalytic potential of ZrBDC MOF for the hydrolysis of SCB and obtained a TRS yield of 0.60 mg/mL.

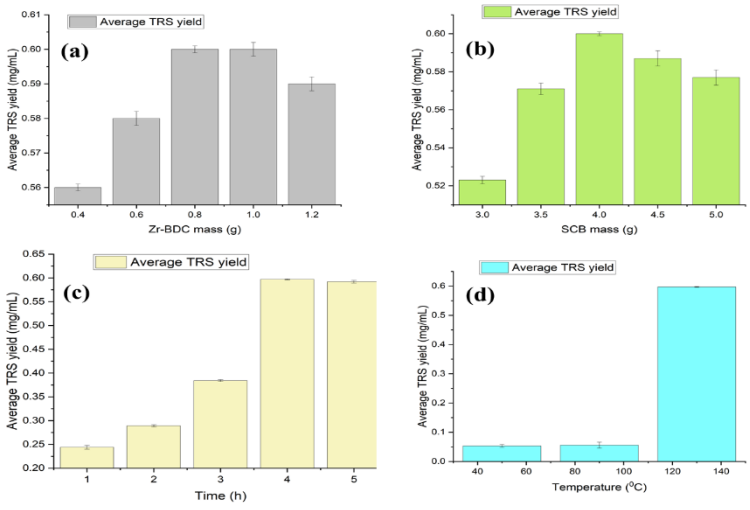

Figure 4. (a) ZrBDC mass optimization for the hydrolysis of SCB, (b) SCB mass optimization for the hydrolysis of SCB, (c) Time optimization for the hydrolysis of SCB, and(d)Temperature optimization for the hydrolysis of SCB.

Optimum parameters for the hydrolysis of pretreated PP

About 4 g of pretreated PP was hydrolyzed with varying amounts of ZrBDC MOF (0.4, 0.6, 0.8, 1, and 1.2 g) at 130 ºC for 4 h to optimize the amount of the catalyst. As shown in Figure 5a, increasing the amount of ZrBDC MOF from 0.4 to 0.8 g resulted in an increase in TRS yield from 0.878 to 2.044 mg/mL. However, a slight decline in TRS yield was observed when the ZrBDC MOF amount exceeded 0.8 g, reaching 1.915 mg/mL. This decrease in TRS content with a further increase in ZrBDC MOF mass might be attributed to additional factors such as the saturation of active sites on the MOF surface or the occurrence of side reactions. It is possible that beyond a certain point, a further increase in ZrBDC MOF mass might lead to the decomposition of sugars into other by-products, resulting in a reduced TRS yield. Therefore, the optimum amount of ZrBDC MOF for maximizing the TRS yield was determined to be 0.8 g.

To get the optimum loading of PP for hydrolysis, the reaction was carried out using the optimum amount of ZrBDC MOF (0.8 g) at 130 ºC for 4 h with varying amounts of PP (3, 3.5, 4, 4.5, and 5 g). As depicted in Figure 5b, the maximum TRS yield of 2.044 mg/mL was obtained at 4 g of PP. A decrease in reducing sugar yield was observed beyond 4 g of PP. This decrease in TRS content may be due to the decrease in the adsorption capacity of the ZrBDC MOF catalyst as a result of high substrate loading that slows down mass transfer phenomena. Thus, the results suggest that 4 g is the optimum amount of PP for the hydrolysis reaction at the given reaction conditions.

To optimize time, hydrolysis was carried out using 4 g of PP and 0.8 g of ZrBDC MOF at 130 ºC varying the time from 1 to 5 h. As shown in Figure 5c, there is a gradual increase in TRS yield from 0.419 to 0.805 mg/mL as the reaction period increases from 1 to 2 h. Beyond 2 h, the reducing sugar yield increases linearly, reaching a maximum TRS yield of 2.044 mg/mL at 4 h. Beyond 4 h, the TRS concentration is almost similar to the TRS concentration obtained at 4 h, but the volume of TRS hydrolysate decreased due to the loss of more water through evaporation. Thus, 4 h is found to be the optimum hydrolysis time, which led to the production of 2.044 mg/mL of TRS.

Different temperatures (50, 90, and 130 ºC) were used for optimization with a one factor at a time approach. So, the hydrolysis was carried out at temperatures of 50, 90, and 130 ºC by keeping ZrBDC MOF mass, PP mass, and time at the optimum values. As indicated in Figure 5d, the TRS yields at 50 and 90 ºC was significantly lower (0.117 and 0.189 mg/mL, respectively) compared to the TRS yield at 130 ºC (2.044 mg/mL). This suggests that the catalytic effect of the ZrBDC MOF is relatively low at temperatures below 100 ºC. However, as the temperature increased beyond 100 °C, the TRS yield increased linearly, reaching a maximum of 2.044 mg/mL at 130 °C. This indicates that ZrBDC MOF exhibits improved catalytic activity for hydrolysis at higher temperatures. Based on the results, 130 ºC was identified as the optimum temperature for hydrolysis under the given conditions. At this temperature, the catalytic effect of ZrBDC MOF was maximized, yielding the highest TRS. It was observed that attempting to carry out the hydrolysis reaction beyond 130 ºC led to the slurry solidifying within a short period of time due to excessive water loss through evaporation before the hydrolysis reaction reach to completion. Therefore, by using these optimized values (0.8 g of ZrBDC MOF, 4 g of PP, 4 h, and 130 ºC) for all four parameters together, the catalytic potential of ZrBDC MOF for hydrolysis of PP was evaluated, resulting in a total reducing sugar (TRS) yield of 2.044 mg/mL.

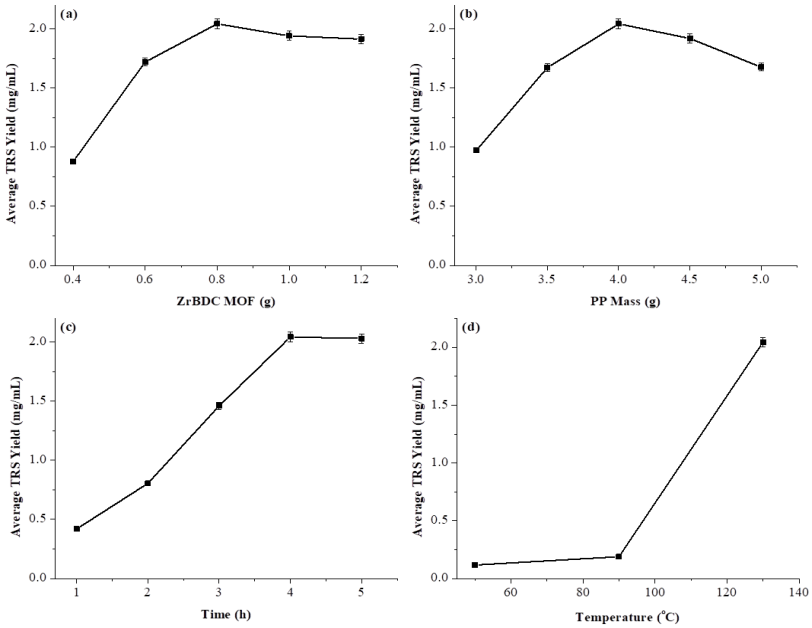

Figure 5. (a) ZrBDC MOF optimization for the hydrolysis of PP, (b) PP mass optimization for the hydrolysis of PP, (c) Time optimization for the hydrolysis of PP, and (d) Temperature optimization for the hydrolysis of PP.

Control sample hydrolysis of SCB and PP

When the hydrolysates for both SCB and PP obtained at the end of the control sample reaction were tested for the presence of TRS by the DNS method, no color change was observed. This implies that TRS was not present in the hydrolysate, indicating that the pretreated SCB and PP were not depolymerized to glucose in the absence of the catalyst. The control sample reactions for both SCB and PP are shown in Figure 6a.

Interestingly, the experimental results indicate that PP conversion to TRS using ZrBDC MOF catalyst is higher as compared to SCB conversion (Figure 6b). This might be due to the presence of less amount of lignin (2.51 %) in the pretreated PP when compared to the lignin (8.12 %) found in the pretreated SCB. Moreover, it might be due to the diffusion of more cellulose from PP than from SCB through the porous system of the ZrBDC MOF to reach the acid sites (open metal sites) of the MOF that could function as Lewis acid sites for catalytic activity [37,38]. The observed catalytic activity of ZrBDC MOF for the hydrolysis of SCB and PP is due to the coordinatively unsaturated open metal site (Zr^{4+} ions) of the framework that can exhibit Lewis acid activity.

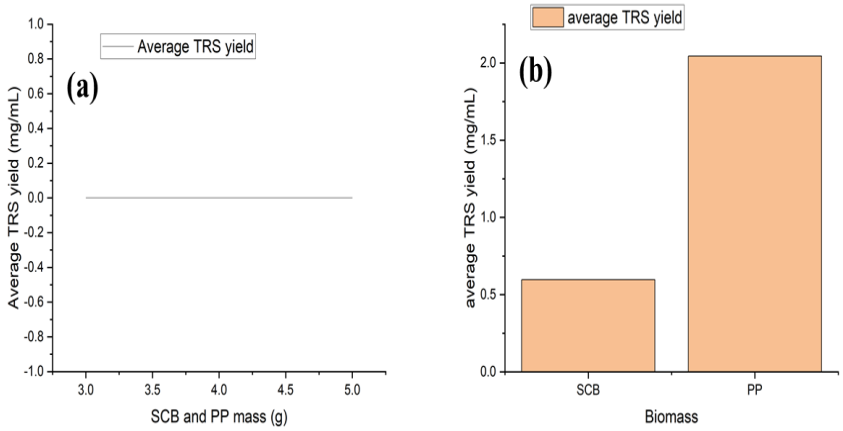

Figure 6. Hydrolysis of varying amounts of pretreated SCB and PP without ZrBDC MOF at 130 ºC for 4 h (a) and hydrolysis yield of SCB and PP (b).

CONCLUSION

The evaluation of ZrBDC MOF as an acid heterogeneous catalyst for the hydrolysis of lignocellulosic biomasses, such as sugarcane bagasse (SCB) and pineapple peels (PP), has shown promising results. The remarkable ability of ZrBDC MOF to function as a catalyst for cellulose hydrolysis can be attributed to the contribution of Lewis acid sites provided by the unsaturated zirconium centers present in the MOF framework, especially under the optimized reaction conditions. In the case of SCB hydrolysis, 4 g of SCB were subjected to hydrolysis using 0.8 g of ZrBDC MOF as the catalyst. The reaction was carried out at 130 ºC for 4 h, resulting in a total reducing sugar (TRS) yield of 0.60 mg/mL. This indicates that ZrBDC MOF demonstrates catalytic activity in breaking down the cellulose present in SCB and to release reducing sugars. Similarly, when 4 g of PP was hydrolyzed using 0.8 g of ZrBDC MOF as the catalyst at 130 ºC for 4 h, a higher TRS yield of 2.044 mg/mL TRS was obtained. This further confirms the ability of ZrBDC MOF to catalyze the hydrolysis of cellulose in lignocellulosic biomasses, leading to the production of significant amounts of reducing sugars. The results indicate that ZrBDC MOF holds promise as a catalyst for cellulose hydrolysis in both SCB and PP, highlighting its potential for biomass conversion and the production of valuable products such as reducing sugars. Therefore, the usage of water as the sole solvent, lower energy requirements (room temperature), a shorter synthesis time (1 day) for the preparation of ZrBDC MOF, and an efficient catalyst-to-substrate ratio make the findings of this study economically feasible and environmentally friendly for the hydrolysis of real lignocellulosic biomasses, such as sugarcane bagasse (SCB) and pineapple peels (PP).

Data availability statement

Our data are included in this manuscript, and, if necessary, other research data will be made available upon reasonable request to the corresponding author, Jemal M. Yassin.

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