Article

Chemoenzymatic Conversion of Biomass-Derived *D*-Xylose to Furfuryl Alcohol with Corn Stalk-Based Solid Acid Catalyst and Reductase Biocatalyst in a Deep Eutectic Solvent–Water System

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Abstract: In this work, the feasibility of chemoenzymatically transforming biomass-derived *D*-xylose to furfuryl alcohol was demonstrated in a tandem reaction with SO_4^{2-}/SnO_2-CS chemocatalyst and reductase biocatalyst in the deep eutectic solvent (DES)–water media. The high furfural yield (44.6%) was obtained by catalyzing biomass-derived *D*-xylose (75.0 g/L) in 20 min at 185 °C with SO_4^{2-}/SnO_2-CS (1.2 wt%) in DES ChCl:EG–water (5:95, *v/v*). Subsequently, recombinant *E. coli* CF cells harboring reductases transformed *D*-xylose-derived furfural (200.0 mM) to furfuryl alcohol in the yield of 35.7% (based on *D*-xylose) at 35 °C and pH 7.5 using HCOONa as cosubstrate in ChCl:EG–water. This chemoenzymatic cascade catalysis strategy could be employed for the sustainable production of value-added furan-based chemical from renewable bioresource.

Keywords: furfural; furfuryl alcohol; biological reduction; *D*-Xylose; *E. coli* CF

1. Introduction

With the rapid consumption of fossil-fuels, together with the growing global warming and environmental concerns, lignocellulosic biomass is regarded as ideal and promising alternative for producing biofuels and bio-based chemicals [1,2]. Biomass or biomass-derived *D*-xylose has been industrially used for the production of furfural (FAL) with acid catalyst via dehydration reaction [1,3]. FAL is used in the production of furans, such as furfuralcohol (FOL), furoic acid (FA), etc. [4–6]. It has a wide range of applications in various industries, such as medicine, agriculture, chemicals, and cosmetics [7–9]. Recently, most catalytic production of FAL has used a variety of heterogeneous solid acid, such as sulfonated tin-based zeolite, sulfonated diamond powder (S-DP) and del-Nu-6(1) [4,5]. S-DP converted biomass-derived *D*-xylose to FAL with 76% yield at 200 °C in 5 min. Catalyst del-Nu-6(1) catalyzed the conversion of biomass-derived *D*-xylose to FAL in 47% yield within 4 h at 170 °C. Very recently, there has been great interest in utilizing biomass-based solid acid catalysts using biomass as carriers for the production of furfural due to the availability, abundance, and renewability of lignocellulosic materials. Catalyst CST, which was obtained from teff straw by simultaneous carbonization and sulfonation, could dehydrate *D*-xylose (20 g/L) to FAL at 62% yield in 0.5 h at 170 °C [6]. Sulfonated tin-based argil catalyzed *D*-xylose into FAL in the yield of 57% at 180 °C in 20 min [7].

Due to the undesired side-reactions (e.g., FAL decomposition, self-coupling, or resinification) in pure water, several organic solvent–water biphasic media, such as toluene–water, γ-valerolactone (GVL)–water, and methyl isobutyl ketone (MIBK)–water, have been prepared as reaction systems for promoting the formation of FAL and enhancing the productivity of FAL by the extraction in situ of product FAL into the organic phase and separation of FAL from chemocatalysts [10]. In the past few years, unconventional and nonaqueous

solvents such as ionic liquids (ILs) and deep eutectic solvents (DESs) have been designed and prepared to enhance the yields of FAL [11]. DESs can be synthesized by mixing hydrogen bond acceptors (HBAs) (e.g., choline chloride) and a hydrogen bond donors (HBDs) (e.g., amines, carboxylic acids, and polyols), which have gained a considerable interest due to their properties close to those of ILs [12]. As one kind of green and environmentally friendly solvent, DESs have been applied as pretreatment media for dissolving and pretreating lignocellulosic materials, and have been utilized to remove lignin, hydrolyze hemicelluloses, or synthesize FAL [13].

FAL is a versatile molecule for the synthesis of various furan-based chemicals [4,5]. As a value-added FAL derivative, furfuryl alcohol (FOL), which contains a furan substituted with a hydroxymethyl (–CH$_2$OH) group, has been widely used for manufacturing synthetic fiber, rubber resin, furan resin, ascorbic acid, lubricant, lysine, vitamin C, and hypergolic fuel in rocketry [14,15]. According to statistics, 60% of FAL is used to produce FOL. A series of catalysts (e.g., Cu/MgO-Al$_2$O$_3$, Ni-Cu/SiO$_2$, Pt/m-CN-x and, Au/Cu-Al$_2$O$_3$) [16–19] have been employed to prepare FOL from FAL via chemical approach. Although the chemical production of FOL can give high yields and good selectivities, high-energy consumption and environmental issues might limit its application. On the contrary, the biological method is attracting much attention due to its energy-saving and environmentally friendly performance [20–22]. FAL can be converted into FOL by some bacteria (e.g., *B. coagulans* NL01, *B. cereus*, and *E. coli* CF) [7,20,22,23].

In this study, the production of FOL was conducted via chemical-enzymatic cascade conversion of biomass-derived *D*-xylose in a tandem reaction by sequential catalysis with biomass-based solid acid SO$_4^{2-}$/SnO$_2$-CS chemocatalyst and *E. coli* CF whole-cells biocatalyst in DES ChCl:EG–water system. The effects of various chemical reaction parameters (e.g., ChCl:EG dosage, SO$_4^{2-}$/SnO$_2$-CS dose, performance temperature, and catalytic time) on the production of FAL were investigated using biomass-derived *D*-xylose as feedstock. In addition, various biological reduction reaction parameters (e.g., HCOONa loading, performance pH, bio-reduction temperature, metal ion additives, and substrate FAL loading, etc.) were tested on the biotransformation of FAL into FOL using whole-cells of recombinant *E. coli* CF harboring reductase. Finally, one-pot chemical-enzymatic synthesis of FOL from biomass-derived *D*-xylose was demonstrated by sequential dehydration with bio-compatible solid acid SO$_4^{2-}$/SnO$_2$-CS and bio-reduction with recombinant *E. coli* CF cells.

2. Materials and Methods

2.1. Materials and Reagents

Corn stalks (CS) were collected from Lianyungang Farm (Changzhou Jiangsu province, P.R. China). Choline chcloride (ChCl), ethylene glycol (EG), *D*-xylose, glucose, SnCl$_4$·5H$_2$O, sodium formate (HCOONa), NADPH, sulfuric acid (H$_2$SO$_4$), and other chemicals were purchased from Sino pharm Group Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Chemical Conversion of D-Xylose to FAL in ChCl:EG–Water System

The preparation of SO$_4^{2-}$/SnO$_2$-CS solid acid catalyst: milled CS was soaked in H$_2$SO$_4$. The acid-treated CS (AT-CS) was mixed with SnCl$_4$-5H$_2$O and anhydrous ethanol, then ammonia was slowly dripped into the mixture; the resulting colloidal solution was dried in an oven, the dried solid powder was dried after sulfonation in dilute H$_2$SO$_4$ and finally calcined in a muffle furnace to obtain SO$_4^{2-}$/SnO$_2$-CS [24].

The conversion of *D*-xylose to FAL with SO$_4^{2-}$/SnO$_2$-CS: in an autoclave reactor, *D*-xylose (3.0 g) and SO$_4^{2-}$/SnO$_2$-CS (0–3.6 wt%) were mixed in 40 mL DES–water media (ChCl:EG, 0–40 v%). This mixture was then blended by stirring (500 rpm) and heated to the desired performance temperature (160–195 °C) for reaction time (10–50 min). After the catalytic reaction was complete, the reactor was allowed to cool down to room temperature in an ice–water cooling bath immediately.

2.3. Bio-Reduction in FAL to FOL with CF Whole-Cells

To enhance the bio-reduction efficiency of CF whole-cells, several biological reaction factors were investigated on the biotransformation of *D*-xylose-derived FAL. To investigate the effect of ChCl:EG loading on the bio-reduction activity, CF wet cells (0.050 g/mL) were incubated 40 mL DES–water (DES ChCl:EG dosage 0–40 v%) were blended with *D*-xylose-derived FAL (200.0 mM), HCOONa (3.0 mol HCOONa/mol FAL), and NADPH (1.0 μmol NADPH/mol FAL) at 35 °C. To evaluate the effect of the amount of cosubstrate HCOONa on bio-reduction activity, different amounts of HCOONa (HCOONa/FAL = 0–5/1 mol/mol) were loaded to 40 mL DES–water (ChCl:EG 5 v%, pH 7.5) with *D*-xylose-derived FAL (200.0 mM), CF wet cells (0.050 g/mL), and NADPH (1.0 μmol NADPH/mol FAL) at 35 °C. To test the effect of temperature and pH on the biocatalytic activity, *D*-xylose-derived FAL (200.0 mM) and CF wet cells (0.050 g/mL) were incubated in 40 mL DES–water (ChCl: EG 5 v%, pH pH 5.0–9.5) containing HCOONa (3.0 mol HCOONa/mol FAL) and NADPH (1.0 μmol NADPH/mol FAL) at 25–50 °C. To evaluate the effect of metal ion additives on bio-reduction activity, several metal ions (Sn^{4+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, and Li^+) (0.50 mM) were separately added to 40 mL DES–water (ChCl:EG 5 v%, pH 6.5) with *D*-xylose-derived FAL (200.0 mM), CF wet cells (0.050 g/mL), HCOONa (3.0 mol HCOONa/mol FAL), and NADPH (1.0 μmol NADPH/mol FAL) at 35 °C. To evaluate the effect of Sn^{4+} on the bio-reduction activity, different doses of Sn^{4+} (0–5.0 mM) were added to 40 mL DES–water media (pH 7.5) with *D*-xylose-derived FAL (200.0 mM), CF wet cells (0.050 g/mL), HCOONa (3.0 mol HCOONa/mol FAL), and NADPH (1.0 μmol NADPH/mol FAL) at 35 °C. The contents of FAL and FOL were determined by HPLC.

2.4. Analytical Methods

The yield of FAL from *D*-xylose was calculated by the following formula:

$$\text{FAL yield (\%)} = \frac{\text{FAL produced (mM)}}{D - \text{Xylose (mM)}} \times 100\% \tag{1}$$

The FOL yield was obtained using the below equation:

$$\text{FOL yield (\%)} = \frac{\text{FOL produced (mM)}}{\text{Initial FAL (mM)}} \times 100\% \tag{2}$$

Furan-based compounds (e.g., FAL and FOL) were measured with HPLC (LC-2030C 3D SHIMADZU, Kyoto, Japan) equipped with reverse-phase C18 (Discovery C18, 3.9 mm ×150 mm, 4 μm) (Bellefonte, PA, USA), which were eluted by 0.4% $(NH_4)_2SO_4$/CH_3OH (95:5, *v/v*) at a flow rate of 0.6 mL/min. FAL and FOL were assayed at 254 and 210 nm, respectively.

3. Results and Discussion

3.1. Optimization of Conditions for FAL Production

DESs have been utilized in the sustainable chemical processes due to their unique properties [25], which have been regarded as a green cosolvent to promote the generation of FAL in the aqueous system [22]. It is very likely that the established DES–water media can facilitate the formation of FAL molecules and prevent the undesired degradation or cross polymerization of FAL [24]. In this study, DES (ChCl:EG) was used as additive for the establishment of ChCl:EG–water media for catalyzing *D*-xylose into FAL. The volumetric ratio of ChCl:EG to water phase had a profound effect on the dehydration of *D*-xylose. Different loading of ChCl:EG were separately mixed with water to form various ChCl:EG–water media. In 40 mL aqueous media, the ChCl:EG dosage was varied as 0–40 v%. The synthesis of FAL was carried out by using SO_4^{2-}/SnO_2-CS as catalyst at 185 °C for 20 min. As illustrated in Figure 1a, as the ChCl:EG loading increased from 0 to 5 v%, the FAL yield were gradually raised. When the ChCl:EG dose reached 5 v%, the yield of FAL was 44.6%. By increasing ChCl:EG content from 5 to 40 v%, the FAL yields decreased considerably. Thus, the optimum ChCl:EG loading was 5 v%. When the DES ChCl:EG loading increased

in ChCl:EG–water, it was very likely that the rehydration and degradation reaction of FAL would be weakened. However, an excessive addition of ChCl:EG might reduce the contact opportunity of substrate *D*-xylose to catalyst SO_4^{2-}/SnO_2-CS, which would result in the decreased FAL yields.
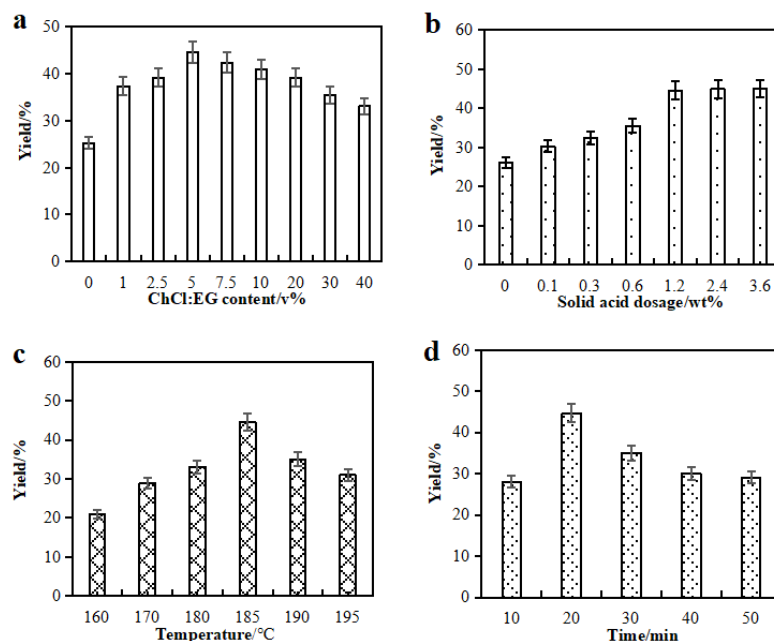

Figure 1. Effects of DES ChCl:EG (0–40 v%) on the FAL production via *D*-xylose dehydration (**a**); Effects of solid acid dose (0–3.6 wt%) on the FAL production via *D*-xylose dehydration in ChCl:EG–water (5:95, *v/v*) (**b**); Effects of dehydration temperature (160–195 °C) on the FAL production via *D*-xylose dehydration in 20 min in ChCl:EG–water (5:95, *v/v*) (**c**); Effects of dehydration time (10–50 min) on the FAL production via *D*-xylose dehydration at 185 °C in ChCl:EG–water (5:95, *v/v*) (**d**).

To further promote the FAL yields, it is necessary to obtain the optimum reaction conditions [26,27]. In ChCl:EG–water (5:95, *v/v*), SO_4^{2-}/SnO_2-CS loading (0–3.6 wt%), performance temperature (160–195 °C), and reaction time (10–50 min) were optimized using *D*-xylose as feedstock. Upon raising SO_4^{2-}/SnO_2-CS dose from 0 to 1.2 wt%, the FAL yields gradually increased (Figure 1b). The highest yield of FAL reached 44.6%. When the SO_4^{2-}/SnO_2-CS loading was raised from 1.2 wt% to 3.6 wt%, FAL yields had no significant change. Thus, the optimum dose of SO_4^{2-}/SnO_2-CS was 1.2 wt%. When *D*-xylose dehydration reactions were culminated at diverse dehydration reaction time (10, 20, 30, 40 and 50 min) and diverse reaction temperature (160, 170, 180, 185, 190, and 195 °C), the highest FAL yield was obtained at 185 °C in 20 min (Figure 1d). Moreover, the conversion rate of xylose to FAL was 96.0%. Higher temperatures (190–195 °C) resulted in a lower yield of FAL, probably because higher temperatures accelerated the occurrence of undesired side-reactions. Clearly, SO_4^{2-}/SnO_2-CS catalyzed dehydration of *D*-xylose into FAL (223.0 mM) in the highest yield of 44.6% in ChCl:EG–water (5:95, *v/v*).

3.2. Optimization for Bio-Reduction in FAL to FOL

The bio-reduction in carbonyl compounds into alcohols has attracted considerable interest due to the product specificity, mild reaction, and high efficiency [7,28–30]. To effectively transform FAL to FOL with CF cells in ChCl:EG–water, various parameters (e.g., cosubstrate HCOONa, bio-reduction pH, bio-reduction temperature, metal ion additives, cell dosage, etc.).

　　　　Upon raising the HCOONa concentration from 0 to 3 mol HCOONa/mol FAL, the catalytic activity gradually increased (Figure 2a). By increasing HCOONa loading from 3 to 5 mol HCOONa/mol FAL, the biocatalytic activity gradually decreased. It is likely that the viscosity of reaction media increased so that the FAL reducing activity decreased. Thus, the appropriate molar ratio of cosubstrate HCOONa to FAL was 3:1. Biocatalytic temperature had a profound influence on the FOL formation. The biocatalytic activity increased with the increase in reaction temperature from 25 to 35 °C. High bio-redcution activity was observed at 35 °C (Figure 2b). When the performance temperature exceeded 35 °C, the reductase activity dropped considerably, possibly due to the thermal deactivation of reductase in whole-cells during the bio-reduction [2,7]. Significantly, the optimal reaction temperature was 35 °C. By increasing the reaction pH from 5.0 to 7.5 at 35 °C, the biocatalytic activity reached the highest value (Figure 2c). Over pH 7.5, the biocatalytic activity decreased clearly. Thus, the optimum reaction pH was 7.5.
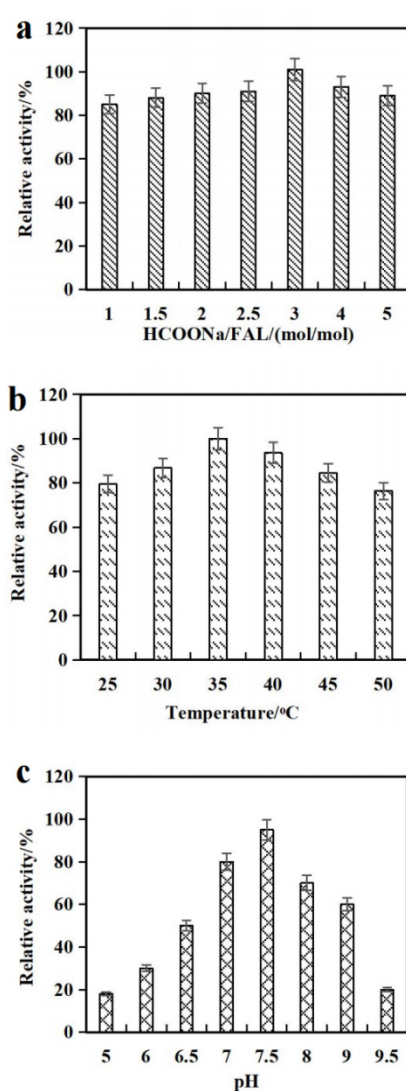

Figure 2. The effect of HCOONa-to-FAL molar ratio on the FAL-reducing activity (**a**); The effect of bioreaction temperature on the FAL-reducing activity (**b**); The effect of bioreaction pH on the FAL-reducing activity (**c**).

　　　　The effects of various metal ions (0.50 mM) on the reductase activity were also examined in the ChCl:EG–water at 35 °C and pH 7.5. Metal ions types and dosages could significantly influence the activities of alcohol dehydrogenases [31]. In this study, $SnCl_4$, $ZnCl_2$, $CoCl_2$, $FeCl_3$, $MnCl_2$, $FeCl_2$, $AlCl_3$, $CaCl_2$, $CuCl_2$, $MgCl_2$, and LiCl (0.50 mM) were

separately added into bio-reduction system. Clearly, Mg^{2+} and Li^+ inhibited the reductase activity. While Sn^{4+}, Zn^{2+} Co^{2+}, and Fe^{3+} could significantly promote the reductase activity (Figure 3a). Sn^{4+} could give the highest reductase activity. During the utilization of SO_4^{2-}/SnO_2-CS, element Sn might be dissolved in the reaction system. The effects of different loading of Sn^{4+} (0–5.0 mM) on the bio-reduction activity were also tested. It was observed that 0.1–0.8 mM Sn^{4+} could be promote reductase activity. Clearly, the optimal Sn^{4+} dose was 0.50 mM, and the reductase activity of CF cells was increased by 1.2-fold compared to the control in the absence of Sn^{4+} (Figure 3b). By increasing Sn^{4+} dosage from 0.9 to 5.0 mM, the activity gradually dropped from 2.1% to 17.9%. These results indicated that Sn^{4+} and SO_4^{2-}/SnO_2-CS were compatible towards reductase in CF whole-cells to some extent. From the view of biochemical aspect, this property would facilitate the chemoenzymatic conversion of biomass-derived *D*-xylose into FOL without removal Sn^{4+} and SO_4^{2-}/SnO_2-CS. To further enhance the FAL-reducing activity, the combination of Sn^{4+} and other metal ion (Zn^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+} or Mn^{2+}) on conversion of FAL with *E. coli* CF is under progress.
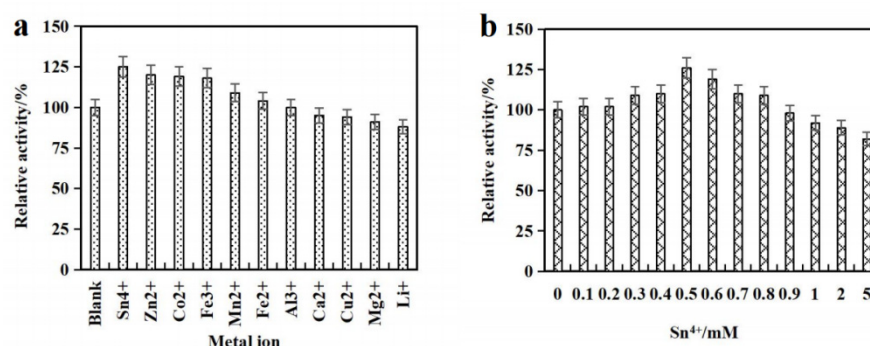

Figure 3. The effect of metal ion additives on the FAL-reducing activity (**a**); The influence of Sn^{4+} dosage on the FAL-reducing activity (**b**).

Furthermore, the CF cell dosage might have significant influence on the FOL yield. As illustrated in Figure 4, the FOL formation clearly increased with increased cell dosage from 0.025 to 0.050 (wet weight)/mL. At 0.050 g/mL, 150 mM FAL could be completely catalyzed into FOL. By increasing CF cell dosage from 0.050 to 0.075 g/mL, no significant change was observed on the FOL yield. Over 0.075 g/mL, the FOL yield dropped gradually. It is likely that the high-loading of cells might cause the increase in the reaction system's viscosity, and the FOL yield significantly decreased.
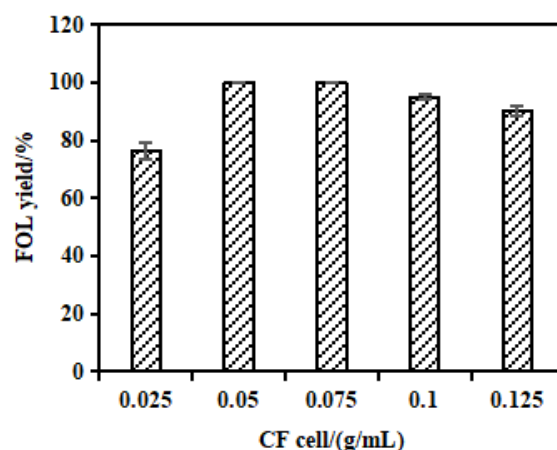

Figure 4. The effect of CF cell dosage on the FOL yield (150 mM FAL, 35 °C, pH 7.5, 0.50 mM Sn^{4+}, 8 h).

3.3. Chemical-Enzymatic Conversion of D-Xylose into FOL

In the past few years, chemical-enzymatic cascade catalysis has been applied to synthesize highly value-added chemicals [32]. In the DES-water system, catalysis of *D*-xylose to FAL with SO_4^{2-}/SnO$_2$-CS and bio-reduction in FAL to FOL with recombinant *E. coli* CF were combined into the transformation of *D*-xylose to FOL in a cascade reaction manner. In an autoclave reactor containing 40 mL ChCl:EG–water (5:95, *v/v*) at 185 °C, 3.0 g *D*-xylose could give 223.0 mM FAL in 20 min. Then, after adjusting pH value to 7.5, the FAL liquor A obtained was diluted with KPB (100 mM, pH 7.5) to form FAL liquor B (50–200 mM FAL). *E. coli* CF whole cells (0.050 g/mL), Sn^{4+} (0.50 mM), HCOONa (3.0 mol HCOONa/mol FAL), and NADPH (1.0 μmol NADPH/mmol FAL) were added to initiate the bioconversion of FAL liquor B at 35 °C. Time courses for the bioconversion of dilute *D*-xylose-derived FAL (50–200 mM) were monitored (Figure 5). It was found that 50–100 mM FAL could be completely converted into FOL at 35 °C within 6 h, while 150 mM FAL could be fully catalyzed to FOL within 8 h. At 200 mM, FOL was obtained in the yield of 80.0%. Conversion of *D*-xylose to FOL in 35.7%–44.6% yield (based on *D*-xylose) was conducted via sequential catalysis with SO_4^{2-}/SnO$_2$-CS and CF cells in ChCl:EG–water system. Compared with previous reports [14,33], this strategy could be used to utilize FAL for FOL production within a relatively short reaction time. In this study, an effective chemical-enzymatic strategy for transforming *D*-xylose to FOL via sequential SO_4^{2-}/SnO$_2$-CS catalysis and CF whole-cell bio-reduction was successfully demonstrated.

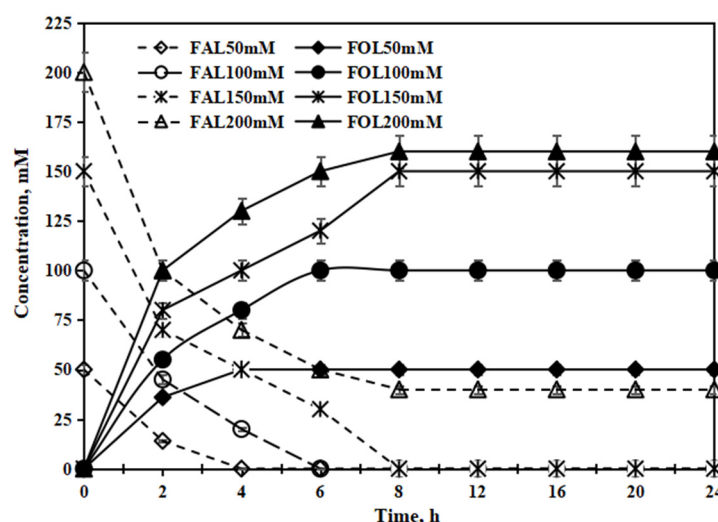**Figure 5.** Time courses for the bio-reduction in *D*-xylose-derived FAL (50–200 mM) by whole cells in the presence of HCOONa (3.0 mol HCOONa/mol FAL).

This study provided a tandem catalytic process for chemoenzymatically valorizing *D*-xylose to FOL in one same autoclave reactor (Figure 6). This process might cut down the equipment input and reduce the usage of solvents (e.g., water and DES). The concentration of FAL in this tandem catalytic process was not very high, by using *D*-xylose as feedstock. The FAL yield need to be drastically enhanced for the efficient production of FOL. Besides the effectiveness of catalysts for high yield and high selectivity in the formation of products, solvents also play an important role in enhancing products yield [34,35]. DESs are inexpensive, easy to prepare, lower toxicity and environmentally friendly solvents, which have been utilized to conduct chemocatalysis and biocatalysis reactions [36–39]. This combined chemical-enzymatic strategy for tandemly transforming *D*-xylose to FOL by SO_4^{2-}/SnO$_2$-CS and *E. coli* CF whole-cells in DES ChCl:EG–water. HCOONa was chosen as the cosubstrate for the bio-reduction in FAL into FOL. Compared with glucose as cosubstrate [27,31], this developed process using HCOONa as cosubstrate was regarded as greener approach in the industrial applications [40]. From the view of industrial biotechnology applications, it was of great interest to develop a cost-effective process

for the enhancement of FAL production [27,41], and to further promote FOL formation with high reductase activity. This established one-pot chemoenzymatic strategy might facilitate the conversion of biomass resource into value-added furan-based chemicals in an environmentally friendly reaction media.
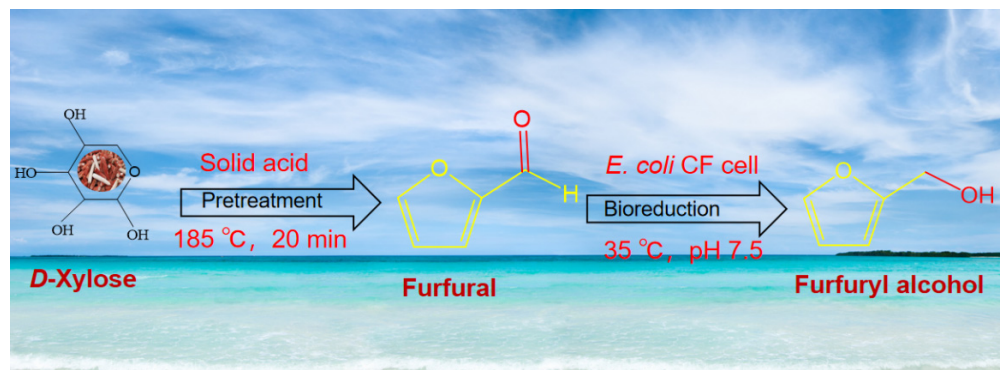

Figure 6. Tandem catalysis for chemoenzymatically valorizing *D*-xylose to FOL.

4. Conclusions

In the *D*-xylose dehydration, high FAL yield (44.6%) was achieved by catalyzing *D*-xylose (75.0 g/L) with SO_4^{2-}/SnO_2-CS (1.2 wt%) in DES ChCl:EG–water (5:95, *v*/*v*) at 185 °C within 20 min. Subsequently, *E. coli* CF whole cells could convert *D*-xylose-derived FAL (50–200 mM) into FOL in the yield of 80–100% (based on FAL) within 8 h at 35 °C and pH 7.5 using HCOONa as cosubstrate. The one-pot conversion of *D*-xylose to FOL at 35.7%–44.6% yield (based on *D*-xylose) was conducted via sequential catalysis with SO_4^{2-}/SnO_2-CS and CF cells in ChCl:EG–water. This combined catalytic strategy provides an environmentally friendly idea for the conversion of biomass-derived *D*-xylose to FOL.

Author Contributions: Conceptualization, Methodology and Writing original draft, J.L. and L.J.; Data curation, J.H.; Software, S.T.; Supervision, Review and revising manuscript, Y.H. All authors have read and greed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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