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Upcycling of Waste Poly(ethylene terephthalate) into 2,4-Pyridine Dicarboxylic Acid by a Tandem Chemo-Microbial Process

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ABSTRACT: This study presents a chemo-microbial cascade process for the upcycling of waste poly(ethylene terephthalate) (PET) into valuable compound 2,4-pyridine dicarboxylic acid (2,4-PDCA). Initially, waste PET undergoes efficient hydrolysis to terephthalic acid (TPA) with a high yield of 92.36%, catalyzed by *p*-toluenesulfonic acid (PTSA). The acid catalyst exhibits excellent reusability, maintaining activity over five cycles. Subsequently, a one-pot, two-step whole-cell conversion system utilizing genetically modified *Escherichia coli* strains (*E. coli* PCA and *E. coli* 2,4-PDCA) converts the generated TPA into 2,4-PDCA. By integrating the PET hydrolysis module with the 2,4-PDCA biosynthesis module, the study achieves an impressive overall efficiency of 94.01% in converting challenging PET waste into valuable 2,4-PDCA. Our research presents a rational design strategy for PET upcycling and 2,4-PDCA synthesis methods. This research provides a systematic approach to PET upcycling, demonstrating its feasibility and potential for industrial application.

Keywords: Poly(ethylene terephthalate); Plastic upcycling; Chemo-microbial process; 2,4-Pyridine dicarboxylic acid

1. Introduction

The extensive utilization of plastics has become an integral part of modern life [1,2]. However, the accumulation of non-biodegradable plastic waste in landfills and oceans has reached alarming levels [3,4]. A potential solution to plastic pollution is the creation of a circular economy for plastics [5–7].

Among the various types of plastics, poly(ethylene terephthalate) (PET) stands out as a major contributor to global plastic pollution due to its widespread use [8–12].

Energy recovery, physical recycling, and chemical recycling are three conventional recycling strategies for PET recycling. Energy recovery mainly consists of incineration or pyrolysis of PET, leading to environmental pollution. Physical recycling involves the grinding and remelting of PET into secondary plastics, which are both considered downcycling processes as lower-value products are produced. Chemical recycling of PET involves depolymerization of TPA and EG and followed by repolymerization of TPA and EG to produce virgin PET or another polymer [13,14]. According to previous research, the cost of recycling PET waste-derived EG and TPA into PET again is $1.3–1.5/kg, suffering from limited economic efficiency [15,16]. Therefore, identifying effective technical solutions is crucial for advancing toward a circular plastic economy. Biotechnology holds significant promise for advancing plastic recycling efforts, as recognized in recent research [17–19]. In particular, engineered microorganisms have been employed to convert the PET monomer TPA into valuable chemicals [15,16,20,21]. It is worth noting that these studies have highlighted the importance of PCA, an intermediate compound derived from TPA. PCA has been demonstrated to possess notable antioxidant and anti-inflammatory properties and has shown potential as an antihyperglycemic and neuroprotective agent [22,23]. Furthermore, PCA is involved in the breakdown of lignin, although the complex structure of lignin necessitates intricate pretreatment and separation procedures prior to PCA cleavage and upcycling [24–26]. In order to address these challenges, it is a good technological way to integrate TPA biodegradation pathways with PCA cleavage pathways to streamline pretreatment and enhance valuable product production.

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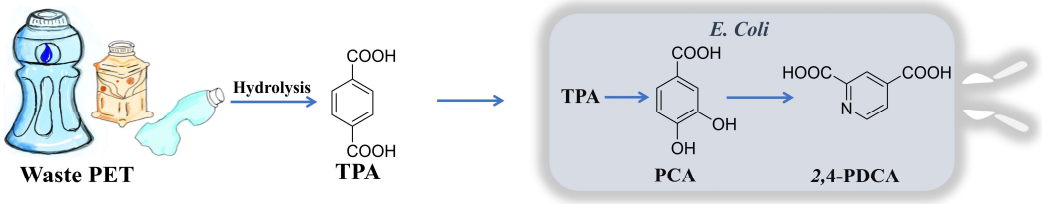
2,4-Pyridine dicarboxylic acid (2,4-PDCA) possesses substantial value in various industries, including coordination chemistry [27,28], the polymer industry [29] and medicinal chemistry [30,31]. It commands a price of approximately $300/kg (https://api.chemicalbook.com, 26 June 2024) due to its versatile applications. It serves as a chemical analogue of TPA, presenting potential as a substitute in the production of bio-based plastics [32–34]. Moreover, the value of 2,4-PDCA is competitive compared with other PET high-value products[15,21,35,36].

Traditionally, 2,4-PDCA was synthesized by the oxidation of 2,4-Lutidine, which suffers from low product yield and harsh reaction conditions [37]. Some researchers have reported the bioproduction of 2,4-PDCA from lignin derivatives. Timothy D.H. Bugg rerouted the PCA meta-cleavage pathway by insertion protocatechuate 4,5-dioxygenase or protocatechuate 2,3dioxygenase into R. jostii RHA1, 80–125 mg/L 2,4-PDCA yield was obtained in 1% wheat straw lignocellulose [33]. The productivity of 2,4-PDCA was increased by 5-fold in engineered *Pseudomonas putida* KT2440 strains using a resting-cell-based bioprocess, as reported by Eduardo Díaz's group [32]. While there have been documented methods for bioproducing 2,4-PDCA from lignin, there are currently no reported approaches for utilizing PET-derived TPA as the sole substrate for 2,4-PDCA production. This indicates a research gap and an opportunity to explore and develop novel bioprocessing strategies for the direct conversion of PET-derived TPA into 2,4-PDCA.

This study achieved a breakthrough by integrating chemical hydrolysis with whole-cell bioconversion in a cascade process (Scheme 1). The approach involved depolymerizing PET into TPA through hydrolysis catalyzed by PTSA (*p*-toluenesulfonic acid). Following this, TPA monomers were transformed into 2,4-Pyridine dicarboxylic acid (2,4-PDCA) using metabolically engineered whole-cell *E. coli* strains. This novel strategy for PET upcycling marks a significant advancement in plastics recycling.



Scheme 1. Waste PET upcycling strategy in this work.

2. Materials and Methods

2.1. Materials

Transparent, colorless waste PET was obtained from a PET bottle (Figure S1) purchased from a local supermarket and cut into 2 mm × 2 mm pieces. *p*-toluenesulfonic acid (PTSA, ≥99%), Terephthalic acid (TPA, 99%), Protocatechuic acid (PCA, ≥97%), Ammonium chloride and (NH_4Cl, ≥99.5%) and 2,4-Pyridine dicarboxylic acid (2,4-PDCA, ≥98%) were purchased from Macklin (Shanghai, China). Tris-Hcl (≥99.5%)was purchased from Amresco (Solon, OH, USA).

E. coli BL21 (DE3) was used for molecular cloning and whole-cell bioconversion. Cloning was performed using Gibson Assembly. All genes used herein were synthesized by GENEWIZ (Suzhou, China).

2.2. Characterization

The chemical structure characterization of waste PET and produced TPA were analyzed by Powder X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). XRD was obtained on a Rigaku SmartLab SE diffractometer using Cu Kα radiation in a 2θ range of 5–90° with a scanning rate of $2°\cdot min^{-1}$. FT-IR spectra were collected using the Thermo Fisher Scientific Nicolet iS20 (Waltham, MA, USA). ^{1}H NMR and ^{13}C NMR were conducted on a Bruker 600 MHz spectrometer. PCA and 2,4-PDCA were analyzed and quantified by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity II, Santa Clara, CA, USA) equipped with a UV detector and C18 analysis column (WATERS). For HPLC analysis, the mobile phase was 10% (*v*/*v*) acetonitrile and 0.1% (*v*/*v*) trifluoroacetate in ultra-pure water at a flow rate of 0.7 $mL\cdot min^{-1}$ and the UV detector was set at 254 nm.

2.3. Chemical Hydrolysis of Waste PET

A series of PET hydrolysis reactions were conducted to produce TPA for further processing. Initially, 2.5 g of PET pieces, 50 mL of deionized H_2O and a specific quantity of PTSA were added to a 200 mL pressure-tight reactor equipped with a magnetic stirrer. The hydrolysis reactions were conducted at temperatures ranging from 140–170 °C for 1–5 h. After completing the hydrolysis reaction, the mixture was filtered to separate unreacted PET and insoluble TPA. Subsequently, the remaining unreacted PET and insoluble TPA were subsequently washed with 50 mL NaOH solution (1 mol/L), leaving unreacted PET as a residue. Sulfuric acid (5 mL) was then added to the filtrate to precipitate pure TPA. The unreacted PET and TPA precipitate were dried overnight at 60 °C and then weighed. The PET conversion and TPA yield were calculated using Equations (1) and (2), respectively, as follows:

$$\text{PET Conversion} = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

where W_0 represents the initial weight of PET, and W_1 denotes the weight of unreacted PET.

$$\text{TPA Yield} = \frac{W_2}{W_3} \times 100\% \quad (2)$$

where W_2 is the weight of pure TPA produced and W_3 is the theoretical weight of TPA produced. The theoretical weight of TPA produced was calculated using Equation (3) as follows:

$$W_3 = \frac{\text{PET amount (g)}}{192.2\ (\text{g/mol})} \times 166.13\ (\text{g/mol}) \quad (3)$$

The recycling of the catalyst is crucial for process sustainability. In a typical procedure, the reusability of PTSA was evaluated under optimal reaction conditions. After each cycle, the TPA was separated from the solution using filtration, given that it is insoluble in water. Following vacuum filtration to remove TPA, the residual filtrate was used directly for the next cycle. The PET conversion and TPA yield were calculated using Equations (1)–(3).

2.4. Whole-Cell Bioconversion of TPA to PCA (System PCA)

Whole-cell bioconversion of TPA to PCA was conducted using engineered *E. coli* strains harboring pACYC-TphB-TphAabc (*E. coli* PCA) as biocatalysts. Seed cultures were prepared in 5 mL LB media with chloramphenicol (50 μg/mL), and cultivated overnight at 37 °C and 200 rpm. Subsequently, the seed cultures were inoculated in 600 mL LB media and cultivated at 37 °C and 200 rpm. Upon reaching a cell density of 0.4–0.6 optical density at 600 nm (OD_{600}), 0.1 mM isopropyl-β-D-thiogalactopyranoside (IPTG) was added to the cultures and incubated at 16 °C for 24 h. The *E. coli* cells were harvested by centrifugation at 5000× *g* for 5 min at 4 °C, washed twice with 50 mM Tris-HCl buffer (pH 7.0), and resuspended in TG-1 buffer (30 mM Tris-HCl buffer (pH 7.0), 10% (*w*/*v*) glycerol) with TPA. The reactions were performed at 30 °C and 250 rpm.

2.5. Whole-Cell Bioconversion of PCA to 2,4-PDCA (System 2,4-PDCA)

Whole-cell conversion of PCA to 2,4-PDCA was performed using engineered *E. coli* strains 2,4-PDCA, which harbor pET22b-ligAB (*E. coli* 2,4-PDCA) as biocatalysts. The antibiotic is 50 μg/mL Ampicillin. For the whole-cell conversion, the cell pellets were resuspended in 30 mM Tris-HCl buffer (pH 7.0) with PCA and 0.1 M ammonium chloride (NaOH was added to adjust the pH to 8). The reactions were performed at 30 °C and 250 rpm.

3. Results and Discussion

3.1. Hydrolysis of PET

Before the valorization of PET into high-value products, depolymerization into TPA is a crucial step. In this study, PTSA is used as the acid catalyst due to its strong acidity. Subsequently, the effects of catalyst dosage, reaction temperature, and reaction time on PTSA-catalyzed PET hydrolysis are investigated.

Figure 1A demonstrates the impact of PTSA dosage on the PET hydrolysis process. The results indicated a positive correlation between the PTSA dosage and both PET conversion and TPA yield within the dosage range of 2–10 g. This phenomenon can be attributed to the increased availability of hydrogen ions, which facilitate the hydrolysis of PET. It is important to note that PET hydrolysis is an endothermic reaction that requires elevated temperatures to overcome the energy barrier. Figure 1B presents the impact of varying reaction temperatures on PET hydrolysis. The investigation reveals that PET exhibits resistance to degradation at relatively low reaction temperatures, with a minimum of 140 °C.

As the reaction temperature increased, both the PET conversion and TPA yield showed noticeable improvements. At a reaction temperature of 160 °C, the maximum conversion of PET was observed at 96.69%, accompanied by a TPA yield of 93.98%. Further increasing the temperature beyond 160 °C did not lead to a significant improvement in PET conversion or TPA yield, suggesting that 160 °C is the optimal reaction temperature. The influence of reaction time on the PET conversion and TPA yield was examined and illustrated in Figure 1C. A notable increase in both PET conversion and TPA yield was observed when extending the reaction time from 1 h to 2 h. Subsequently, PET conversion and TPA yield increased gradually as the reaction progressed, reaching their peak at 5 h. It is worth noting that TPA has low solubility in water, allowing for easy recovery through filtration. The filtrate produced from PET hydrolysis contains PTSA and can be directly utilized in subsequent hydrolysis reactions. Figure 1D illustrates the consistently high TPA yield observed across multiple reuse experiments, highlighting the sustainability and efficiency of this approach.

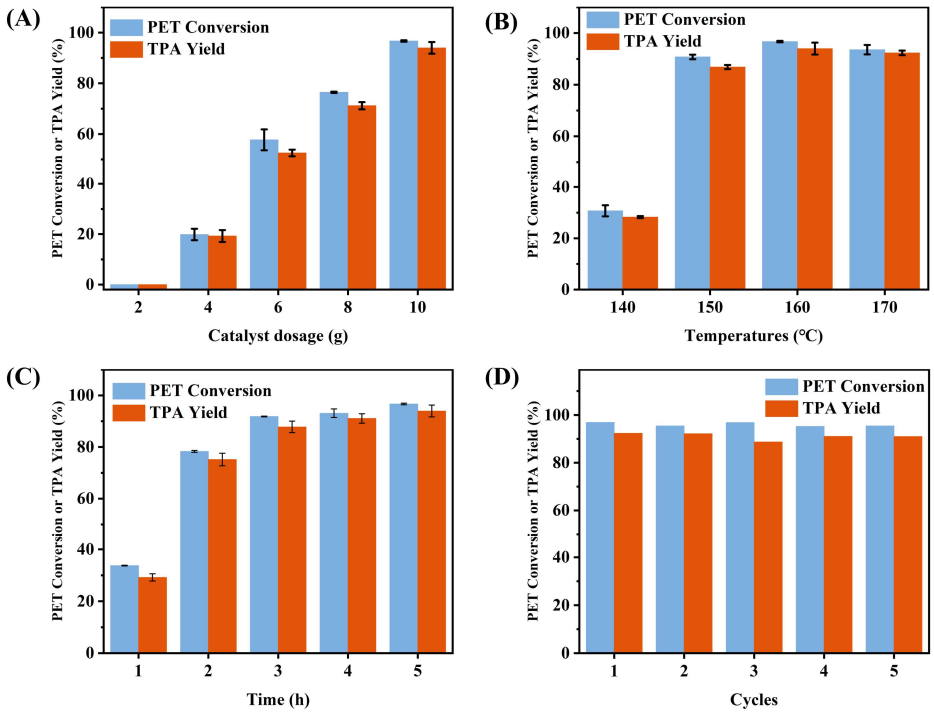


Figure 1. (**A**) Effect of catalyst dosage on PET hydrolysis reaction. Reaction conditions: PET (2.5 g), H_2O (50 mL), 160 °C, 5 h. (**B**) Effect of reaction temperature on PET hydrolysis reaction. Reaction conditions: PET (2.5 g), H_2O (50 mL), catalyst 10 g, 5 h. (**C**) Effect of reaction time on PET hydrolysis reaction. Reaction conditions: PET (2.5 g), H_2O (50 mL), catalyst 10 g, 160 °C. (**D**) recycling and reuse of catalyst for PET hydrolysis. Reaction conditions: PET (2.5 g), H_2O (50 mL), catalyst 10 g, 160 °C, 5 h.

3.2. Characterization of the Produced TPA

The chemical structure of the TPA produced from hydrolysis was investigated by ^{1}H NMR and ^{13}C NMR spectra, as shown in Figure 2. In the ^{1}H NMR spectra, the signal at 8.0 ppm is attributed to the aromatic protons of the benzene ring, while the signal at 13.3 ppm is ascribed to the carboxyl proton. In the ^{13}C NMR spectra, the signals at 129.9 ppm, 134.8 ppm, and 167.1 ppm indicate the aromatic carbon, quaternary aromatic carbon, and carbonyl carbon atoms, respectively. FT-IR was also used to analyze the chemical structure of the PET pieces and the produced TPA. As shown in Figure 2C, the vibration of the benzene ring of PET and TPA can be observed at 1574, 1509 and 1425 cm^{-1}. The C=O stretching vibration and C–O vibration of the ester bonds were observed at 1713 and 1242 cm^{-1}. The peaks at 2000–3500 cm^{-1} can be assigned to the COOH group of TPA. The XRD spectrum of the commercial TPA and the produced TPA showed strong and distinct peaks at 17.3°, 25.1° and 27.8°, confirming the high degree of crystallinity of TPA from the hydrolysis process (Figure 2D). All the characterizations conducted have provided evidence of the high purity of TPA obtained through the PET hydrolysis process.

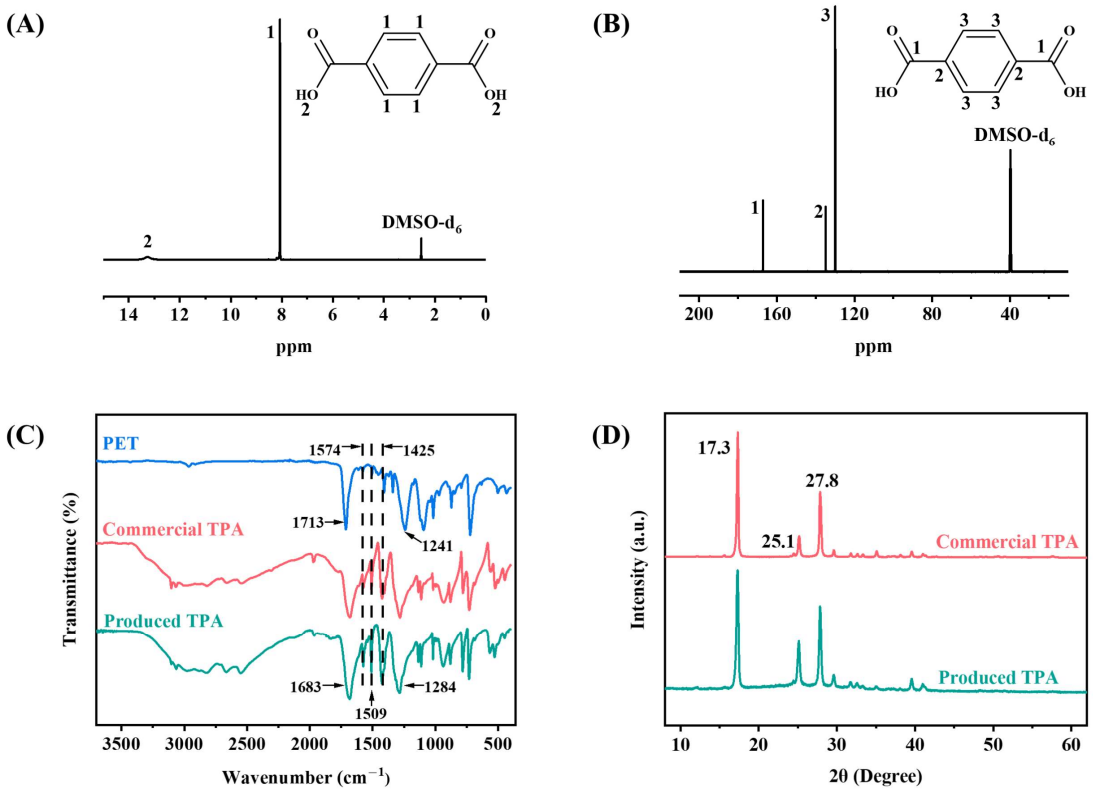


Figure 2. (**A**) ^{1}H NMR spectrum of produced TPA; (**B**) ^{13}C NMR spectrum of produced TPA; (**C**) FT-IR spectra and (**D**) XRD patterns of commercially available TPA and produced TPA from PET hydrolysis process.

3.3. Proposed Mechanism and Process of PET Hydrolysis

The hydrolysis of PET has been the subject of extensive study, with a particular focus on the reaction mechanism catalyzed by an acid catalyst [38–40]. PTSA, which readily undergoes deprotonation in aqueous solutions, plays a crucial role in this process. The presence of hydrogen ions (H^+) facilitates the protonation of the carbonyl carbon within the ester bond of PET. The hydrogen ions interact with the carbonyl groups of PET, resulting in the formation of hydroxyl groups and carbocations. Ultimately, this leads to the forming of the tetrahedral intermediate. Subsequently, the nucleophilic attack by water on the positively charged carbon initiates the cleavage of the ester bond. The specific reaction steps are depicted in Figure 3.

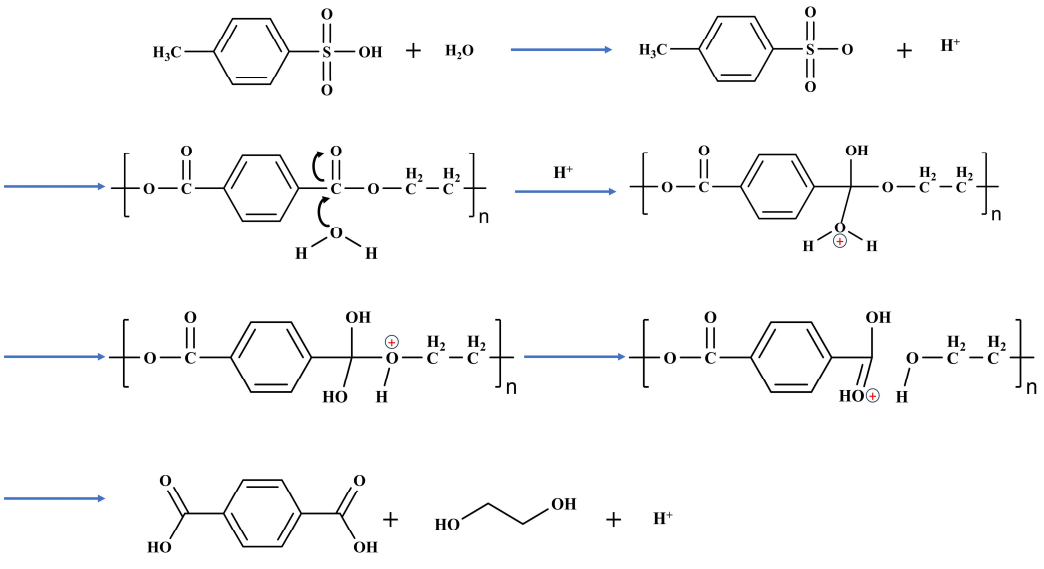


Figure 3. Hydrolysis mechanism of PET catalyzed by PTSA.

3.4. Whole-Cell Conversion of TPA to 2,4-PDCA

To enhance the value-added process of converting TPA, a whole-cell bioconversion was implemented to produce 2,4-PDCA using metabolically engineered *E. coli* strains (Figure 4). The first step involved the transformation of TPA into PCA in *E. coli* strain PCA. This transformation was achieved by introducing two enzymes: TPA 1,2-dioxygenase (encoded by TphAabc) and 1,2-dihydroxy-3,5-cyclohexadiene-1,4-dicarboxylate dehydrogenase (encoded by TphB) from *Comamonas* sp. *E6*.

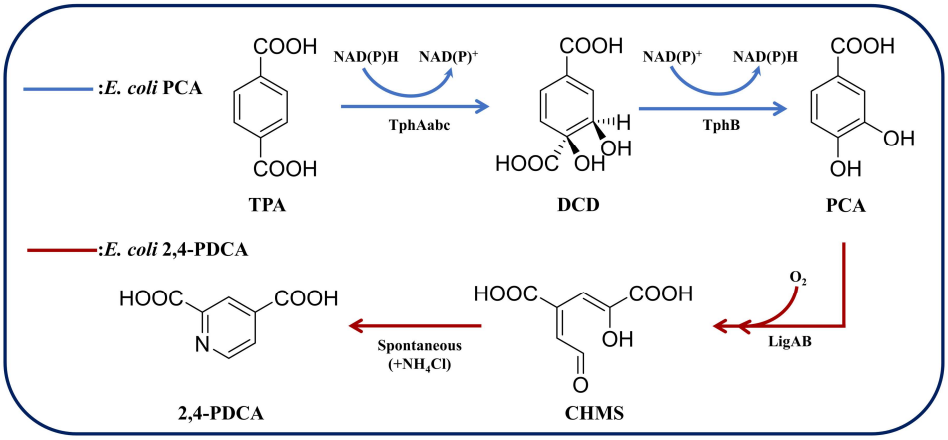


Figure 4. Biosynthetic route of 2,4-PDCA from TPA and the whole-cell conversion strategy using *E. coli* TPA strain and *E. coli* PCA strain.

In order to optimize the production of PCA, an investigation was conducted to assess the effects of inducer concentration and induction time on TPA conversion and PCA yield. The results showed that increasing the concentration of IPTG from 0.05 to 0.1 mM led to a higher PCA yield, reaching a peak and subsequently declining with further increases in IPTG concentration (Figure 5A). A positive correlation was observed between higher inducer concentrations and the formation of inclusion bodies within the total expressed protein, resulting in a reduction in PCA yield [41]. Furthermore, the duration of the induction period was found to impact protein yield and activity significantly. Both insufficient and excessive induction times were associated with a decrease in protein yield and activity (Figure 5B). Based on these findings, 0.1 mM IPTG concentration and 20 h of induction time were selected as the optimal conditions for the subsequent whole-cell conversion of TPA to PCA.

Previous research has indicated the pivotal role of pH in 2,4-PDCA production, attributed to the pH sensitivity of the intermediate 4-carboxy-2-hydroxymuconate-semialdehyde (CHMS) [32,33,42]. Additionally, since the conversion of PCA to 2,4-PDCA involves an oxidation process, oxygen availability also affects the yield of 2,4-PDCA. An investigation into the effect pH on 2,4-PDCA yield revealed that pH values above 8 enhanced the production of 2,4-PDCA (Figure 6A). This finding suggests that maintaining an alkaline pH environment is favorable for the conversion process. To enhance oxygen availability, baffled flasks were used instead of conical tubes, resulting in a slight enhancement in 2,4-PDCA production compared to conical tubes (Figure 6B). This indicates that the oxygen supply plays a role in the yield of 2,4-PDCA, and the use of baffled flasks can help improve its production.

Overall, this study achieved a PCA yield of 89.44% and a 2,4-PDCA yield of 94.01%, demonstrating comparable yields to those obtained using reagent-grade TPA and PCA. These yields are comparable to those obtained using reagent-grade TPA and PCA, demonstrating the feasibility and potential of the combined approach involving chemical hydrolysis and whole-cell bioconversion for producing valuable compounds such as 2,4-PDCA.

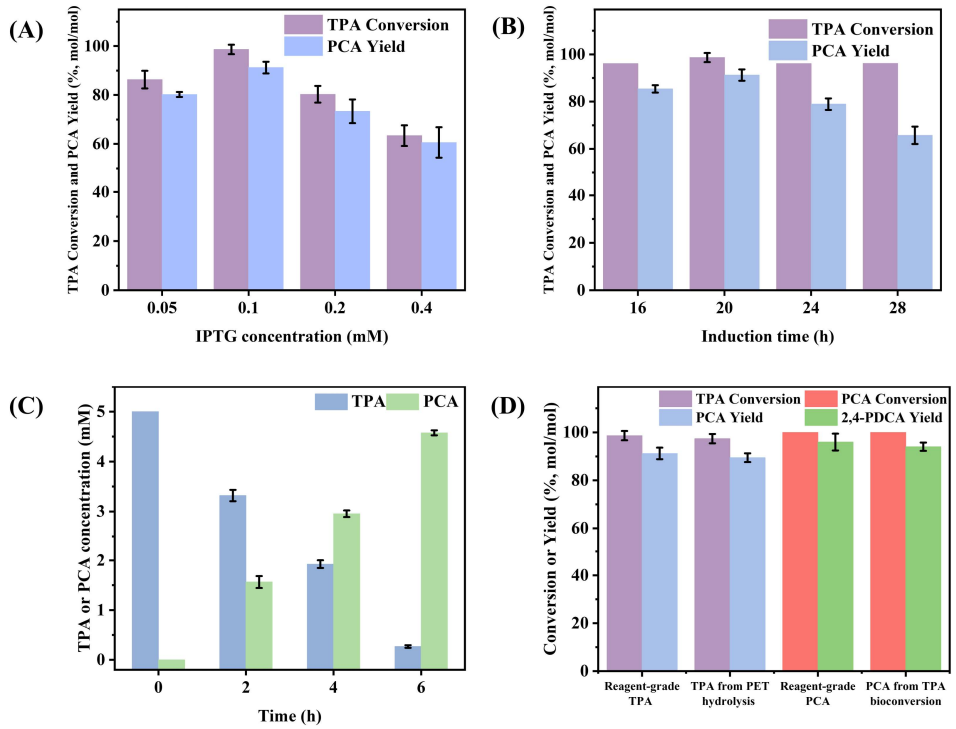


Figure 5. (**A**) Effect of inducer concentration on the synthesis of PCA. Reaction condition: TPA 5 Mm, OD_{600} = 40, Induction time 20 h. (**B**) Effect of inducer time on the synthesis of PCA. Reaction condition: TPA 5 Mm, OD_{600} = 40, IPTG 0.1 mM. (**C**) Effect of reaction time on the synthesis of PCA. Reaction condition: TPA 5 Mm, OD_{600} = 40, Induction time 20 h, IPTG 0.1 mM. (**D**) Production of 2,4-PDCA and PCA from strain *E. coli* PCA and *E. coli* 2,4-PDCA. Reaction condition: TPA 5 Mm, OD_{600} = 40, Induction time 20 h, IPTG 0.1 Mm, reaction time 6 h.

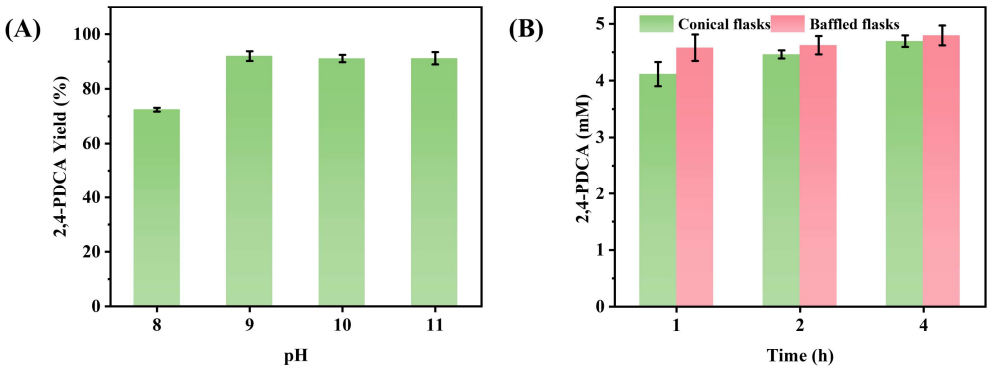


Figure 6. (**A**) Effect of pH on the production of 2,4-PDCA from PCA by strain *E. coli*. Reaction condition: PCA 5 Mm, OD_{600} = 40, reaction time 4 h. (**B**) Comparison of the 2,4-PDCA yield from TPA in different system. Reaction condition: PCA 5 Mm, OD_{600} = 40, pH = 9.

4. Conclusions

In this study, PET was converted to a high-value product 2,4-PDCA through a comprehensive chemo-microbial cascade process. The depolymerization of PET waste into TPA was achieved via a hydrolysis process catalyzed by PTSA, with a yield of 92.36%. Subsequently, a recombinant biocatalysis system involving *E. coli* PCA and *E. coli* 2,4-PDCA yielded 2,4-PDCA with a yield of 94.01%. To further enhance the potential for implementation at an industrial scale, a cost-benefit analysis must be conducted to evaluate the economic viability of adopting the proposed methods at this level, including an assessment of capital investment, operational costs, and the potential for large-scale adoption. In the course of our research, we have discussed the feasibility of a cascade reaction. PCA is an important intermediate chemical for high-value products. Although the price of 2,4-PDCA is considerable, it is not a bulk chemical. In order to enhance the potential of industrial applications, it is essential to develop new, high-value products that are in high demand. However, this research introduces an innovative tandem approach enabling the first-ever production of 2,4-PDCA from PET waste, demonstrating its potential for economically viable PET upcycling.

Supplementary Materials

The following supporting information can be found at: https://www.sciepublish.com/article/pii/371, Figure S1: PET bottle from local supermarket. Table S1: Bacterial strains and plasmids. Table S2: Primers used in this study. Table S3: Gene information used in this study.

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Author Contributions

Z.W.: Writing—original draft, Methodology, Investigation. G.X.: Investigation, Methodology, Project administration, Supervision; Writing—review and editing. Y.L.: Investigation, Data curation. H.S.: Funding acquisition, Methodology, Project administration, Supervision, Writing—review and editing.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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