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# Additive manufacturing-derived free-standing 3D pyrolytic carbon electrodes for sustainable microbial electrochemical production of H<sub>2</sub>O<sub>2</sub>

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### HIGHLIGHTS

### G R A P H I C A L A B S T R A C T

- Pyrolysis of additively manufactured precursors resulted in highly structured 3D carbon.
- 3D pyrolytic carbon (PyrC) electrodes vastly enhanced bioelectrosynthesis of H<sub>2</sub>O<sub>2</sub>.
- H<sub>2</sub>O<sub>2</sub> yield of the 3D PyrC electrode was higher than for conventional electrodes.
- 3D structure offers an abundance of active sites and boosts O<sub>2</sub> mass transfer.
- 3D PyrC electrode showed superior potential for micropollutants elimination.



### ARTICLE INFO

Keywords: 3D printing Pyrolysis Additive manufacturing H<sub>2</sub>O<sub>2</sub> Microbial electrosynthesis

### ABSTRACT

Producing  $H_2O_2$  via microbial electrosynthesis is a cost-effective and environmentally favorable alternative to the costly and environmentally hazardous anthraquinone method. However, most studies have relied on carbon electrodes with two-dimensional (2D) surfaces (e.g., graphite), which have limited surface area and active sites, resulting in suboptimal  $H_2O_2$  production. In this study, we demonstrate the enhanced efficiency of microbial  $H_2O_2$  synthesis using three-dimensional (3D) electrodes produced through additive manufacturing technology due to their larger surface area than conventional carbon electrodes with 2D surfaces. This work innovatively combines 3D printed pyrolytic carbon (3D PyrC) electrodes with highly defined outer geometry and internal mesh structures derived from additive manufacturing with high-temperature resin precursors followed by pyrolysis with microbial electrochemical platform technology to achieve efficient  $H_2O_2$  synthesis. The 3D PyrC electrode produced a maximum of 129.2 mg L<sup>-1</sup> of  $H_2O_2$  in 12 h, which was 2.3–6.9 times greater than conventional electrodes (e.g., graphite and carbon felt). Furthermore, the scalability, reusability and mechanical properties of the 3D PyrC electrode were exemplary, showcasing its practical viability for large-scale applications. Beyond  $H_2O_2$  synthesis, the study explored the application of the 3D PyrC electrode in the bio-electro-Fenton process, demonstrating its efficacy as a tertiary treatment technology for the removal of

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micropollutants. This dual functionality underscores the versatility of the 3D PyrC electrode in addressing both the synthesis of valuable chemicals and environmental remediation. This study shows a novel electrode design for efficient, sustainable synthesis of  $H_2O_2$  and subsequent environmental remediation.

### 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) stands as one of the globally massproduced chemicals, with an anticipated annual production of 6.5 million tons in 2022, catering to diverse industries such as pharmaceuticals, chemicals, environmental applications, and textile bleaching [1]. The unprecedented demand for H<sub>2</sub>O<sub>2</sub>, particularly amid the Covid-19 pandemic, where it has been extensively utilized as a broad-spectrum disinfectant, continues to surge worldwide. The anthraquinone method, utilizing palladium, accounts for over 95% of H<sub>2</sub>O<sub>2</sub> production, but its sustainability is compromised by substantial energy input, waste generation, large-scale plants, and significant capital expenditure [2,3]. The on-site electrochemical synthesis of  $H_2O_2$ employing a two-electron oxygen reduction reaction (2e<sup>-</sup> ORR) at the cathode has recently been identified as a promising alternative technique. Compared to the traditional approaches, this method has the advantages of being more ecologically friendly, having mild operating conditions, and cutting costs on transportation and storage [4]. Despite these benefits, the high electrical energy consumption impedes its large-scale deployment [5].

Microbial electrochemical systems (MES), predominantly the microbial fuel cell (MFC) and its derivative, the microbial electrolysis cell (MEC), which employ electrochemically active bacteria to harvest chemical energy stored in organic matter from wastewater, have recently been extensively studied for cost-effective, sustainable, and onsite  $H_2O_2$  generation [6,7]. The  $H_2O_2$  synthesis process is primarily influenced by the type and properties of the cathode material [4,7,8]. The majority of MES used for on-site H<sub>2</sub>O<sub>2</sub> generation in previous investigations utilize carbonaceous materials with two-dimensional (2D) surfaces as cathodes. Particularly, commercially available carbonaceous materials such as graphite plates and gas diffusion electrodes (GDEs) have been contemplated for their commendable electrical conductivity, stability, chemical resistance, non-toxicity, and cost-effectiveness [8,9]. Despite these merits, graphite plates exhibit inefficiency in H<sub>2</sub>O<sub>2</sub> production attributed to limited surface area and relatively low 2e<sup>-</sup> ORR selectivity [10,11]. While GDEs as cathodes can achieve heightened H<sub>2</sub>O<sub>2</sub> yields due to superior 2e<sup>-</sup> ORR selectivity and mass transfer, their mechanical characteristics pose challenges for scalability, and prolonged operation may lead to notable performance degradation due to hydrophobic layer breakdown [12].

It is widely recognized that augmenting the electrode surface area is critical for large-scale  $H_2O_2$  generation. Compared to conventional electrodes with 2D surfaces, three-dimensional (3D) carbonaceous materials emerge as advantageous candidates for the cathode, given their larger specific surface area, abundant active sites and lower resistivity [8]. Microbial electrochemical techniques utilizing 3D electrodes could improve wastewater treatment efficacy by providing additional active sites through micropores, leading to higher current output than 2D electrodes. This promotes of cathodic  $H_2O_2$  synthesis and anodic COD removal [13].

The recent advancements in additive manufacturing (3D printing) technology offers novel avenues for designing and fabricating 3D electrodes using conductive materials across diverse applications. Additively manufactured 3D electrodes provide distinct advantages including intricate and precise fabrication, efficient reactor design, diminished material waste and energy consumption, and rapid prototyping in comparison to conventional 3D electrodes [14–16]. Zhang et al. demonstrated fused filament fabrication (FFF) with composite materials for 3D printing of flexible graphene circuits [17] while Zhu et al. employed direct-ink writing for patterning of hierarchical

graphene aerogels [18]. However, the production of free-standing 3D electrode structures with complex geometries, small feature resolutions and overall sizes exceeding a few millimeters using traditional 3D printing processes is challenging. Moreover, most of these manufacturing processes are complex and demanding, requiring synthesis of custom-made materials and the use of relatively expensive equipment. A novel and promising microfabrication method has emerged in recent years, combining additive manufacturing and pyrolysis processes to create 3D carbon electrodes [19–21]. This innovative approach allows the production of 3D-engineered carbon structures with intricate geometries, feature sizes with sub-mm dimensions and overall sizes surpassing several centimeters [22].

In this study, we proposed and implemented an innovative, low-cost, fast, and simple approach to fabricate geometrically well-defined 3D pyrolytic carbon (3D PyrC) electrodes for H<sub>2</sub>O<sub>2</sub> synthesis in MES using high resolution stereolithography (SLA) 3D printing followed by pyrolysis. The viability of the 3D PyrC electrode for in situ synthesis of H<sub>2</sub>O<sub>2</sub> was thoroughly examined considering a wide range of parameters, including input voltage, electrode thickness, cathodic aeration velocity, cathodic electrolyte pH, types and concentration. Additionally, the novel 3D PyrC electrode was assessed for the removal of numerous emerging micropollutants from secondary effluent of wastewater treatment plants (WWTPs) by using the bio-electro-Fenton (BEF) process. To the best of our knowledge, the combination of environmentally friendly MES platform technology with highly structured 3D PyrC electrodes prepared via additive manufacturing for enhanced in situ synthesis of H<sub>2</sub>O<sub>2</sub> has never been reported before. The results provide new insights into developing a novel, cost-effective, energy-efficient technology for H<sub>2</sub>O<sub>2</sub> synthesis with simultaneous wastewater treatment.

### 2. Materials and methods

### 2.1. Preparation of 3D pyrolytic carbon electrodes

The concept for fabricating the free-standing 3D PyrC electrodes is illustrated in Fig. 1. A 3D reticular pattern was chosen as a model for meshing the bulk electrodes to significantly increase the electroactive surface area of the electrode and thereby boost the 2e<sup>-</sup> ORR kinetics. The models were designed with Fusion 360 (Education License, V. 2.0.13881, Autodesk, Inc.) software and exported into the 3D printer software (Preform V. 3.26.0 Formlabs Inc.) as a stereolithography (.stl) file. After preliminary experiments, the cubic mesh structures ( $\sim$ 74  $\times$ 43 mm<sup>2</sup> in length and width) with a unit size of 1.5 mm and circular crossbars with a diameter of 350 µm were chosen as the optimum design (Supplementary information, Fig. S1). To examine the scalability, electrolyte diffusability through the depth of the electrode and contribution of the bulk of the 3D PyrC electrodes to the H<sub>2</sub>O<sub>2</sub> production reactions, reticular electrodes with 5, 7 and 9 suspended mesh levels were designed as shown in Fig. 1a resulting in a total 3D print height of 6.2 mm, 9.3 mm, and 12.3 mm, respectively. A schematic illustration of the 3D printing system and the 3D printed structure attached to the build platform are presented in Fig. 1b. After releasing the structure from the build platform and washing for 10 min in fresh isopropanol, a postcuring process was run in a UV exposure chamber for 5 min (405 nm wavelength and 30% intensity, BSL-01, Opsytec Dr Grobel, Germany). The post-cured structure was carbonized in a horizontal ceramic tube furnace (MTI Corp., GSL 1700x) at a constant nitrogen gas flow rate of 200 sccm (Fig. 1b). The sample was located on a stainless steel mesh to achieve more uniform gasification during the pyrolysis process. A pyrolysis process with gradual ramping of the temperature up to 1000°C was employed to control the kinetics of thermal degradation, reduce the decomposition rate and thereby better preserve the shape of the electrode during the pyrolysis process (temperature profile curve is presented in SI, Fig. S1b). A titanium wire with 0.1 mm diameter was used to connect the electrode to the MES reactor.

#### 2.2. Morphology and material properties of 3D PyrC electrodes

The shape and morphology of the 3D PyrC electrodes was characterized using scanning electron microscopy (SEM, Zeiss Supra VP 40, Germany). The crystallinity of the 3D PyrC electrode was studied by Xray diffractometer (XRD, PANalytical, model AERIS X-ray with Cu Ka radiation, beam current of 30 mA,  $\lambda = 1.5406$  Å, voltage=40 kV, Malvern Panalytical Ltd., The Netherlands). X-ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa, USA) was employed to examine the elemental composition and chemical state of the developed 3D PyrC electrode. Raman spectroscopy (micro-Raman system, Thermo Scientific Nexsa, USA) with an excitation wavelength of 532 nm and 8 mW laser power was employed to investigate the presence of any characteristic peaks of graphitic microdomains within the 3D PyrC electrodes. The 3D PvrC electrodes' specific surface area and pore volume were assessed through Brunauer-Emmett-Teller (BET) measurements: N2 adsorption/ desorption data were obtained at 77 K using a NOVATouch LX2 Analyzer (Quantachrome Instruments, USA). Prior to testing, the samples underwent pre-outgassing at 350 °C for 6 h.

### 2.3. MES reactor configuration and operation

A two-chamber (400-mL, total volume) microbial electrochemical reactor made of polycarbonate was developed. The two chambers (8 cm in length, 5 cm in width, and 5 cm in height) were separated by a cation exchange membrane (CMI 7001, Membrane International, NJ). The anode chamber utilized a commercially available carbon brush (5.9 cm in diameter, 6.9 cm in length, Mill-Rose, USA) with a high specific surface area, while the cathode employed a newly developed 3D PyrC electrode. Notably, both the commercial cation exchange membranes and carbon brushes mentioned above must be pretreated before reactor installation, as outlined in our earlier work [6]. The inoculum was obtained from the influent water of a WWTP (Lundtofte, Copenhagen, Denmark), and an additional  $1 \text{ g L}^{-1}$  sodium acetate was added to enrich the electrochemically active bacteria at the anode after assembling the reactor. The reactor was operated in MFC mode throughout this period, with a 1000 ohm resistor connected in series between the anode and cathode. A 50 mM potassium ferricyanide solution containing 50 mM phosphate buffer (pH 7.2) was utilized as the cathodic electrolyte. After one month of anodic enrichment, a mature biofilm formed and produced a steady and repeatable voltage of up to 0.72 V.

The anode chamber was constantly fed with WWTP influent was teamended with sodium acetate (1 g  $\rm L^{-1}$ ). The anode was connected to a 500 mL recirculation bottle through a peristaltic pump, which circulated the anode solution at a rate of 30 mL min<sup>-1</sup> (104 RA-CH.4, OLE DICH, Denmark). The cathode chamber was filled with 180 mL of sodium sulfate solution at a concentration of 50 mM and pH 2. The reactor was operated in batch mode. After that, the effect of different operational parameters such as input voltage, cathodic aeration velocity, catholyte pH, electrolyte nature and electrolyte concentrations on the performance of the novel 3D PyrC electrodes for synthesizing H<sub>2</sub>O<sub>2</sub> were comprehensively evaluated. Finally, the applicability of the 3D PyrC electrode for wastewater treatment was further validated in a bioelectro-Fenton process. Specifically, the WWTPs secondary effluent was spiked with a solution containing 24 micropollutants (Sigma, Denmark) at concentrations ranging from 20 to 130 g L<sup>-1</sup> (see Text S1). The operating parameters of the reactor were set according to the previous H<sub>2</sub>O<sub>2</sub> synthesis experiment, and the ferrous sulfate dosage was 0.2 mM.

### 2.4. Analytical methods

A pH meter was used to determine the pH of all samples (PHM 210, radiometer). A digital DO meter (Multi 3420, WTW, UK) equipped with an optical IDS DO sensor was used to measure the dissolved oxygen (DO) of the catholyte (FDO 925, WTW, UK). As previously reported, the concentration of H<sub>2</sub>O<sub>2</sub> was determined using the spectrophotometric technique (Spectronic 20D+, Thermo, Scientific) [6]. The electrochemical studies were conducted in a 100 mL three-electrode electrochemical setup employing the 3D PyrC electrode as working, an Ag/AgCl in 3 M KCl as reference electrode and a coil of platinum (pt) wire as the auxiliary electrode. Electrochemical analysis of the 3D PyrC electrodes was carried out using an Autolab PGSTAT128N potentiostat/galvanostat in combination with the NOVA program, version 2.1.4 (Metrohm Autolab BV, The Netherlands). Linear sweep voltammetry (LSV) was conducted at a scan rate of 10 mV s<sup>-1</sup>. A high-performance liquid chromatography (Agilent 1290 Infinity, USA, HPLC) system coupled with a tandem mass spectrometer (Agilent 6470 series, USA, MS/MS) was used to quantify the concentration of 24 micropollutants. The detailed operational parameters of the HPLC/MS/MS system are described in Text S2. The system voltage (V) was automatically recorded every 30 min by the data acquisition system (Model 2700, Keithley Instruments, Inc., Cleveland, OH, USA) and the corresponding system current (I) was calculated by Ohm's law. The current efficiency and energy consumption of the system for H<sub>2</sub>O<sub>2</sub> synthesis were calculated according to Text S3.

### 3. Results and discussion

### 3.1. Morphology and material properties of 3D PyrC electrodes



The integration of 3D printing technologies with a pyrolysis process provides a heightened level of flexibility compared to alternative

Fig. 1. Scheme of the fabrication process: (a) CAD model of the (d) a photograph of the 3D PyrC electrode with 5 suspended mesh levels and overall dimensions of  $\sim$  34  $\times$  19  $\times$  5 mm<sup>3</sup> derived from additive manufacturing technology.

structural engineering methods, enabling the fabrication of complex and tailorable free-standing carbon electrodes [22-24]. Here, the utilization of stereolithography 3D printing, coupled with subsequent thermal treatment, facilitated the production of support-free, monolithic, and mechanically robust 3D PyrC electrodes with dimensions extending up to several centimeters. SEM images of the 3D PyrC electrode (Fig. 2a) reveal that the overall reticular pattern was preserved after the pyrolysis process, indicating the uniform isotropic shrinkage of the 3D polymer precursor structure during the thermal treatment process. The electrode had a mesh unit dimension of  $347\pm26\,\mu m$  and the diameter of the circular crossbars was 162  $\pm$  14  $\mu m$  after the pyrolysis process. Moreover, the SEM image with higher magnification (Fig. 2b) demonstrates the presence of very rough topography and porous surfaces which could be attributed to the precursor decomposition and degassing during the pyrolysis process. The electrodes shrunk almost isotropically shrunk in all directions during the pyrolysis process and had the final dimensions of approximately 34 mm  $\times$  19 mm in length and width, and 2.7, 3.8 and 5 mm in height for 5, 7 and 9 mesh levels, respectively. The bulk and surface composition of the as-fabricated 3D PyrC electrodes was investigated using X-ray diffraction and Raman spectroscopy. The diffraction pattern of the 3D PyrC electrode in Fig. 2c reveals that the pyrolyzed photopolymer had a semi-crystalline nature with two broad peaks located at about 23.5 and 43.5 corresponding to the (002) and (100) diffraction patterns of the graphitic and disordered carbon phases, respectively. This confirms the formation of pseudo graphitic carbon in line with results reported by others [25,26]. Moreover, the higher intensity of the G peak (at 1590 cm<sup>-1</sup>, representing crystalline graphite) than the D peak (at 1360  $\text{cm}^{-1}$ , representing disordered carbon) in the Raman spectrum (I<sub>G</sub>/I<sub>D</sub>≈1.1, Fig. 2d) suggests that the 3D PyrC electrode had a slightly higher fraction of graphitic than disordered carbon [27,28]. In addition, the observed broad 2D peak around 2800  $cm^{-1}$ reveals that the graphitic microdomains with more than few layers were randomly oriented within the bulk of the 3D PyrC electrode. The

chemical composition of the as-pyrolyzed 3D PyrC electrode was assessed by XPS (Fig. 2e). The XPS spectrum revealed that the surface only contained carbon and oxygen elements and their atomic percentages were 93.6% and 6.4%, respectively. The high-resolution XPS spectrum in the region of C 1 s (Fig. 2f) consisted of signals corresponding to the C-C bond (sp<sup>3</sup> hybridization at 285.6 eV), C=C bond (sp<sup>2</sup> hybridization at 284.4 eV) and different carbon to oxygen bonds. The considerably large ratio of sp<sup>2</sup>/sp<sup>3</sup> hybridizations also affirmed the graphitic nature of the pyrolyzed 3D structured material [29,30].

### 3.2. Microbial electrosynthesis of H<sub>2</sub>O<sub>2</sub> using 3D PyrC electrodes

### 3.2.1. Microbial electrosynthesis of $H_2O_2$ with different designs of 3D PyrC electrodes

The 3D printing process used in this study was the SLA technique, where a laser beam cures photopolymer resin and builds the 3D model of the electrode layer by layer. The number of printed layers directly determines the specific surface area and the number of mesh levels of the subsequent 3D electrode generated by pyrolysis, which may ultimately affect the performance of the 2e<sup>-</sup> ORR process for H<sub>2</sub>O<sub>2</sub> generation [31]. However, pursuing a higher specific surface area and increasing the number of micropores does not invariably align with enhanced H<sub>2</sub>O<sub>2</sub> production. Some studies indicate that H<sub>2</sub>O<sub>2</sub> is more likely to be further reduced on the surface of porous carbon materials with a higher specific surface area, such as a carbon black particle electrode, thereby resulting in a greater loss of H<sub>2</sub>O<sub>2</sub> than on a graphite particle electrode with a smoother, lower surface area [13]. Therefore, the influence of the number of mesh levels printed with the precursor resin during electrode preparation on the efficiency of H<sub>2</sub>O<sub>2</sub> generation in the MES was investigated. 3D PyrC electrodes with 5, 7 and 9 mesh levels were prepared as illustrated in Fig. 1a. Notably, due to the size limitation of the printer itself, the maximum number of printed mesh levels was set to 9.



Fig. 2. Morphology and material properties of 3D PyrC electrode. SEM images of the surface morphology with (a) low and (b) high magnification, (c) XRD pattern, (d) Raman spectrum, (e) XPS survey spectrum and (f) high-resolution spectrum for the C 1 s region.

The experiments were conducted in catholyte of 50 mM Na<sub>2</sub>SO<sub>4</sub>, at pH 2, with 0.4 V input voltage, and aeration velocity of 0.2 mL min<sup>-1</sup> mL<sup>-1</sup>. Fig. 3a shows that for all three designs significant electrosynthesis of H<sub>2</sub>O<sub>2</sub> was measured after 12 h confirming the applicability of the novel 3D PyrC electrodes in this MES. Surprisingly, the quantity of H<sub>2</sub>O<sub>2</sub> produced in the dual-chamber MES reactor increased considerably as the number of mesh levels of the 3D PyrC electrode increased, reaching 94.1, 110.1, and 129.2 mg  $L^{-1}$  for 5, 7 and 9 mesh levels, respectively. Furthermore, more mesh levels of the electrodes were correlated with higher currents (Fig. S2), which means that more electrons were engaged in  $2e^-$  ORR and thus in more  $O_2$  reduction to  $H_2O_2$  [6,11]. Consequently, the computed current efficiencies were 61.7%, 58.3% and 51.5%, respectively (Fig. S2). In particular, the overall geometric surface areas of the 3D PyrC electrodes were estimated by using ImageJ software (National Institute of Health, USA) from the top- and side-views of SEM images. The geometric surface areas of the 3D PyrC electrodes with 5, 7 and 9 mesh levels were calculated to be  $\sim$ 56.9, 79.8 and  $102.6 \text{ cm}^2$ , respectively, while the geometric surface area for a graphite electrode with the same outer dimensions is around 18.3 cm<sup>2</sup>. Moreover, the significantly higher concentration of H<sub>2</sub>O<sub>2</sub> generated from 3D PyrC electrodes could also be attributed to the rough surface topography of their microstructures, which further enhances the electrode/media interface and thereby provides more active sites for electrochemical reactions. In addition, we further supplemented the BET testing to measure the 3D PyrC electrode's specific surface area, validating the exceptional surface area of the 3D PyrC electrode we prepared. The results indicate that the total BET surface area and pore volume of the 3D PyrC electrode are 19.6 m<sup>2</sup> g<sup>-1</sup> and 0.02 cm<sup>3</sup> g<sup>-1</sup>, respectively. Such elevated values of BET surface area and pore volume provide additional active sites, thereby enhancing the synthesis of H<sub>2</sub>O<sub>2</sub>. Remarkably, the cumulative H<sub>2</sub>O<sub>2</sub> output of the 3D PyrC electrodes for all numbers of printed mesh levels grew linearly as running time increased, demonstrating that the functionality of the 3D PyrC electrodes was stable for all designs. Based on these results, 3D PyrC electrodes with 9 mesh levels were further used in this study.

### 3.2.2. Comparison with microbial electrosynthesis of $H_2O_2$ at conventional carbon electrodes

Subsequently, we compared the performance of the 3D PyrC electrode in synthesizing  $H_2O_2$  to that of graphite, carbon felt, carbon cloth, and GDE, all commonly used electrode materials. The characterization of these conventional electrode has been intensively studied in the past [10,32–34]. Fig. 3b depicts the fluctuation in  $H_2O_2$  concentration in the MES reactor as a function of operating time utilizing the various cathode materials. Regardless of the electrode material used, the concentration of accumulated  $H_2O_2$  at the cathode increased linearly with operating time. The most  $H_2O_2$  after 12 h was collected utilizing the novel 3D PyrC electrode, reaching 129.2 mg L<sup>-1</sup>, followed by GDE, carbon cloth, carbon felt, and graphite at concentrations of 55.6, 35.1, 22.6, and 18.8 mg L<sup>-1</sup>, respectively (Fig. 3b). These results clearly reveal that the

novel 3D PyrC electrode outperforms the conventional 2D electrodes for direct electrosynthesis of H<sub>2</sub>O<sub>2</sub> by 2e<sup>-</sup> ORR. The evolution of the system current was well correlated with H2O2 generation and the ORR current obtained with the novel 3D PyrC electrode was much higher than for the other carbon electrodes (Fig. S3a). Accordingly, the current efficiencies of the novel 3D PyrC electrode, GDE, carbon cloth, carbon felt, and graphite were 61.7%, 40.6%, 29.7%, 23.7%, and 23.4%, respectively (Fig. S3b). Also, steady output current validated the stability of the anode (Fig. S3a). These results indicate superior catalytic properties of the 3D PyrC electrode regarding ORR and better electrical conductivity. The fast H<sub>2</sub>O<sub>2</sub> synthesis observed with 3D PyrC electrodes can be primarily attributed to the large specific surface area and porous microstructure with interconnected channels of this novel 3D PyrC electrode providing extra 2e<sup>-</sup> ORR sites and enhanced O<sub>2</sub> mass transfer. This allows O2 to react on the inner surfaces of the electrode, ultimately resulting in a substantial increase in H<sub>2</sub>O<sub>2</sub> production [13,35,36].

$$O2 + 2H + + 2e - \rightarrow 2H2O2 \tag{1}$$

Furthermore, blank experiments, encompassing the MES reactor with an abiotic anode and open circuit conditions, were conducted, with the corresponding results illustrated in Fig. 3. As anticipated, no  $H_2O_2$  production was observed in the open circuit mode, as indicated by Eq. (1), where the absence of electron flow from the anode to the cathode resulted in the absence of  $H_2O_2$  generation (Fig. S3a). Similarly, the presence of  $H_2O_2$  remained undetectable when an abiotic anode was used, which was apparently attributed to the lack of anode electroactive microorganisms to provide electrons and the inability of the cathode to undergo the  $2e^-$  ORR (Fig. S3a).

The results suggest that the 3D PyrC electrode with the MES reactor can consistently furnish sustainable and highly efficient on-site  $\rm H_2O_2$  generation.

### 3.3. Working mechanism

As described above, a two-chamber MES reactor composed of a microbial anode and a novel 3D PyrC cathode was successfully constructed and used for simultaneous anodic wastewater treatment and cathodic insitu synthesis of the green oxidant  $H_2O_2$ . Here, we will briefly discuss the overall working mechanism of the MES as illustrated in Scheme 1. In this MES system, the 3D PyrC cathode and microbial anode are combined to convert biological energy from wastewater into electricity, which is further utilized for the conversion of oxygen into  $H_2O_2$ . At the anode of the MES, organic compounds in urban wastewater are decomposed by electrochemically active microorganisms (typically Geobacter spp.) adhering to the carbon brush electrode surface and producing electrons, protons, and carbon dioxide (Eq. (2)).

$$C_aH_bO_c + (2a-c)H_2O \rightarrow aCO_2 + (b+4a-2c)H^+ + (b+4a-2c)e^-$$
 (2)

The generated electrons and protons are then transferred to the



Fig. 3. Microbial electrosynthesis of  $H_2O_2$  using 3D PyrC electrodes. (a) Microbial electrosynthesis of  $H_2O_2$  with different designs of 3D PyrC electrodes (b) Blank experiments and comparison of cathodic microbial electrosynthesis of  $H_2O_2$  for 3D PyrC electrodes with different conventional carbon electrode materials.



Scheme 1. Schematic of microbial electrosynthesis of  $H_2O_2$  in a dual-chamber MES reactor using a 3D PyrC electrode.

cathode via wires and cation exchange membranes, respectively, where they combine with oxygen molecules on the surface and inside the 3D PyrC cathode via  $2e^-$  ORR (Eq. (1)) to form H<sub>2</sub>O<sub>2</sub>. The significantly higher direct electrosynthesis of H<sub>2</sub>O<sub>2</sub> on the novel 3D PyrC electrodes compared to conventional 2D carbon electrodes (e.g., graphite and GDE) could be attributed to their very rough surface and specific geometry. The 3D mesh and porous carbon surface enhance entrapment of air bubbles on the surfaces and within the bulk of the 3D structure, leading to more oxygen-saturated surfaces and thereby more  $2e^-$  ORR. Furthermore, the higher  $2e^-$  ORR rate at the 3D PyrC electrode increases the MES system current, thereby accelerating anodic organic compound degradation.

### 3.4. Influence of operational factors on microbial electrosynthesis of $\rm H_2O_2$

### 3.4.1. Input voltage

While MES is acknowledged as an environmentally sustainable

electrochemical device capable of harnessing electrical energy from wastewater, its energy consumption cannot be disregarded due to the necessity of an externally applied input voltage (typically below 0.8 V) during prolonged operation in the MEC mode. Furthermore, the quantity of H2O2 synthesis in the MEC mode does not necessarily exhibit proportionality to the input voltage, as higher inputs may inadvertently stimulate side reactions that compromise the current efficiency of the system, resulting in H<sub>2</sub>O<sub>2</sub> generation equivalent to or even inferior to that achieved at lower input voltages [37,38]. Therefore, the influence of input voltage on H<sub>2</sub>O<sub>2</sub> generation was explored further. Additionally, the capacity of the system for synthesizing H<sub>2</sub>O<sub>2</sub> in MFC mode (input voltage of 0 V) was also investigated. Four voltages (0, 0.2, 0.4, and 0.6 V) were utilized to explore H<sub>2</sub>O<sub>2</sub> synthesis. The other operating parameters comprised starting catholyte of 50 mM Na<sub>2</sub>SO<sub>4</sub>, pH 2, and aeration velocity of 0.2 mL min<sup>-1</sup> mL<sup>-1</sup>. Fig. 4a shows that the  $H_2O_2$ concentration increased linearly over 12 h, and that the cumulative  $H_2O_2$  concentration was 57.8, 73.3, 129.2, and 85.3 mg L<sup>-1</sup> for input voltages ranging from 0 to 0.6 V, respectively. Similar findings with a



Fig. 4. Effect of input voltage (a), pH (b), cathodic aeration rate (c), and catholyte type (d), on  $H_2O_2$  production in a dual-chamber MES reactor using a 3D PyrC electrode.

tendency of an initial increase and subsequent drop of the cathodic accumulated  $H_2O_2$  for increasing voltage were observed when graphite was used as cathode [6,39,40]. Moreover, the system's operational current is steady and increases with higher input voltage (Fig. S4a). In contrast, Fig. S4 shows that current efficiency varied following  $H_2O_2$  output, with values of 82.3%, 55.8%, 61.7%, and 26.3% for voltages ranging from 0 to 0.6 V, respectively. Firstly, increasing the voltage from 0 to 0.6 V increases the charge transfer on the cathode, resulting in higher currents. This enhances the cathodic 2e<sup>-</sup> ORR process to form  $H_2O_2$  (Eq. (1)) [6,10,11]. However, higher currents may also trigger the onset of a number of side reactions through Eqs. (3)–(6) [6,41,42].

$$H2O2 + 2H + + 2e \rightarrow 2H2O \tag{3}$$

$$2H2O2 \rightarrow O2 + 2H2O \tag{4}$$

 $O2 + 4H + + 4e - \rightarrow 2H2O \tag{5}$ 

$$2H + + 2e - \rightarrow H2 \tag{6}$$

Notably, despite the small dimensions of the electrode, the system generated a relatively high concentration of  $H_2O_2$  while operating in MFC mode, meeting the need for dosing  $H_2O_2$  (normally ranging from 10 to 50 mg L<sup>-1</sup>) in the  $H_2O_2$  mediated water treatment process (e.g., UV/ $H_2O_2$  process). The high yield of  $H_2O_2$  without extra input voltage achieved with the 3D PyrC electrode will make subsequent water treatment processes utilizing this generated  $H_2O_2$  more affordable.

### 3.4.2. Initial catholyte pH

It has been reported that pH has an effect on the 2e<sup>-</sup> ORR kinetics at carbon material electrodes, hence ultimately influencing the H2O2 production [1]. In this part, the effect of initial pH values of 2, 3, 7, 9 and 11 on H<sub>2</sub>O<sub>2</sub> generation was studied. Other operating parameters comprised starting electrolyte concentration of 50 mM Na<sub>2</sub>SO<sub>4</sub>, 0.4 V voltage, and aeration velocity of 0.2 mL min<sup>-1</sup> mL<sup>-1</sup>. As illustrated in Fig. 4b, the initial pH showed a considerable impact on the efficiency of cathodic microbial electrosynthesis of H<sub>2</sub>O<sub>2</sub>, with corresponding cumulative concentrations reaching 129.2, 32.8, 20.6, 11.3 and 10.0 mg  $L^{-1}$ , respectively, throughout 12 h of operation. Moreover, the current efficiencies were calculated to be 61.7%, 14.6%, 9.7%, 6.5%, and 5.8%, respectively (Fig. S5a and Fig. S5b). Obviously, it was advantageous to run under acidic conditions (pH 2) to obtain more H<sub>2</sub>O<sub>2</sub>. Notably, the accumulated H<sub>2</sub>O<sub>2</sub> at the cathode chamber did not rise linearly with time when the starting pH was 3 or higher but instead had a tendency to increase faster initially before declining.

In acidic electrolytes, the ORR favors the  $2e^-$  route, whereas at higher pH, hydrogenation is hindered, and  $4e^-$  ORR dominates [43]. Furthermore,  $H_2O_2$  is primarily present in the form of  $HO_2^-$  in alkaline catholyte, which has been shown to react with  $H_2O_2$  to consume the remaining  $H_2O_2$  in the solution via Eq. (7) for pH > 11.6 [44,45]. Indeed, the  $H_2O_2$  concentration in Fig. 4b started to decrease after such alkaline conditions were reached for starting pH 3–9 (Figure. S5c).

$$H2O2 + HO2 \rightarrow OH - + O2 + H2O$$
(7)

In addition, the performance of the electrode in synthesizing  $H_2O_2$ under neutral conditions was investigated by maintaining the pH of the cathodic electrolyte at 7, as illustrated in Fig. 4b. There, the accumulated  $H_2O_2$  reached around101 mg L<sup>-1</sup> after 12 h, which was close to the concentration achieved at the initial pH value of 2 and significantly higher than at other initial pH values. These results demonstrate that the novel 3D PyrC electrode can efficiently synthesize  $H_2O_2$  under both acidic and neutral conditions.

### 3.4.3. Cathodic aeration rate

In addition to voltage and pH, dissolved oxygen (DO), is a significant factor for the production of  $H_2O_2$  at the 3D PyrC electrode, as shown by Eq. (1). Typically, the electrochemical synthesis processes of  $H_2O_2$  rely

on a high rate of aeration (air or pure  $O_2$ ) to maintain an oxygensaturated solution and assure maximal H<sub>2</sub>O<sub>2</sub> production [37]. However, rapid aeration rates, which maintain the saturation or even supersaturation of DO in the catholyte, tend to diminish H<sub>2</sub>O<sub>2</sub> generation while increasing energy consumption. The optimal aeration rate maximizes H<sub>2</sub>O<sub>2</sub> generation and reduces costs. Thus, aeration velocities varying from 0 to 0.04 mL min<sup>-1</sup> mL<sup>-1</sup> were selected to explore their effects on H<sub>2</sub>O<sub>2</sub> generation. According to Fig. 4c, after 12 h, the accumulated  $H_2O_2$  concentrations were 25.0, 90.0, 129.2, and 107.0 mg L<sup>-1</sup> for the aeration velocities of 0, 0.01, 0.02, and 0.04 mL min  $^{-1}$  mL  $^{-1},$ respectively. It is evident that cathodic aeration can greatly enhance the synthesis of H<sub>2</sub>O<sub>2</sub> compared to no aeration. The poor system performance without aeration is explained by a distinctly unsaturated catholyte, while it becomes saturated or supersaturated when the aeration rate approaches or surpasses 0.02 mL min<sup>-1</sup> mL<sup>-1</sup> (Fig. S6a) resulting in increased mass transfer [46]. Furthermore, the recorded system currents under aeration conditions are significantly higher than without aeration (Fig. S6b). This further validates the above explanation of to enhance mass transfer with aeration. There might be several reasons for the adverse effects caused by raising the aeration velocity from 0.02 to  $0.04 \text{ mL} \text{min}^{-1} \text{ mL}^{-1}$ . On the one hand, increasing the aeration velocity increases the quantity and size of bubbles generated by the aeration head, which enhances the internal resistance of the system and reduces  $H_2O_2$  generation [47–49]. On the other hand, higher aeration velocity may perturb catholyte-electrode mass transfer, reducing 2e<sup>-</sup> ORR efficiency [50]. These findings show the necessity of controlling cathodic aeration in MES with 3D PyrC electrode for producing H<sub>2</sub>O<sub>2</sub>.

#### 3.4.4. Catholyte type and concentration

Since the conductivity of water is low, electrosynthesis of H<sub>2</sub>O<sub>2</sub> needs supporting electrolytes to enhance the current and achieve effective synthesis. Therefore, we explored the impact of common salts such as Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaNO<sub>3</sub> as electrolytes on the performance of microbial electrosynthesis of H<sub>2</sub>O<sub>2</sub> using the novel 3D PyrC electrode [51]. The operational parameters comprised 50 mM concentrations of each electrolyte, pH of 2, aeration velocity of  $0.02 \text{ mLmin}^{-1} \text{ mL}^{-1}$ , and applied voltage of 0.4 V. As seen in Fig. 4d, the nature of the catholyte had a considerable impact on H2O2 accumulation. Specifically, the accumulation of  $H_2O_2$  over 12 h was 129.2, 82.0, and 85.3 mg L<sup>-1</sup> for Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaNO<sub>3</sub>, respectively, demonstrating that the use of Na<sub>2</sub>SO<sub>4</sub> as the catholyte is most favorable for H<sub>2</sub>O<sub>2</sub> generation. The poorer performance using the other two electrolytes can be explained by unwanted interactions of the electrolyte ions with the synthesized H<sub>2</sub>O<sub>2</sub>. For NaCl as an electrolyte, Cl<sup>-</sup> can consume the formed H<sub>2</sub>O<sub>2</sub> in an acidic environment via Eqs.(8)-(12) [52]. For NaNO<sub>3</sub> as an electrolyte, part of the  $NO_3^-$  may be reduced to  $NO_2^-$  (Eq. (13)) [53], followed by  $H_2O_2$  oxidation of the produced  $NO_2^-$  to  $NO_3^-$ , resulting in the loss of H<sub>2</sub>O<sub>2</sub> via Eq. (14) [54].

$$H_2O_2 + 2 H^+ + 2Cl^- \rightarrow Cl_2 + 2 H_2O$$
 (8)

$$H_2O_2 + H^+ + Cl^- \rightarrow ClO^- + H_2O$$
 (9)

$$H_2O_2 + ClO^- \rightarrow Cl^- + O_2 + H_2O$$
 (10)

$$ClO^{-} \rightarrow O^{-} + Cl \tag{11}$$

$$Cl + H_2O_2 \rightarrow HO_2 + H^+ + Cl^-$$
(12)

$$NO_3^- + 2e^- + 2 H^+ \rightarrow NO_2^- + H_2O$$
 (13)

$$NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O$$
 (14)

Furthermore, since  $H_2O_2$  formed under neutral and alkaline circumstances is unstable and susceptible to additional decomposition, we evaluated the performance of  $H_2O_2$  production utilizing  $Na_2SiO_3$  as an electrolyte at neutral pH of 7, because it is a well-known  $H_2O_2$  stabilizer [3,51]. As shown in Fig. 4d, the  $H_2O_2$  produced in the  $Na_2SiO_3$  catholyte (77.1 mg L<sup>-1</sup> at pH of 7) was significantly elevated compared to  $Na_2SO_4$ 

(20.6 mg L<sup>-1</sup> at pH of 7, Fig. 4b). This is mostly attributed to the stabilizing role of Na<sub>2</sub>SiO<sub>3</sub>, which may limit H<sub>2</sub>O<sub>2</sub> decomposition and increase 2e<sup>-</sup> ORR efficacy [51]. Specifically, the higher polarity of SO<sup>2</sup><sub>4</sub> renders the OOH\* intermediate more stable and reduces H<sub>2</sub>O<sub>2</sub> selectivity and yield [51].

The dosage of the supporting electrolyte affects operational costs, and synthesis of H2O2 with high concentrations of electrolytes increases future purification expenses. Therefore, we further evaluated the influence of varying Na<sub>2</sub>SO<sub>4</sub> concentrations ranging from 10 to 100 mM on the performance of H<sub>2</sub>O<sub>2</sub> production. As depicted in Figure. S7, the dosage of Na<sub>2</sub>SO<sub>4</sub> substantially impacts the system performance. When the concentration of Na<sub>2</sub>SO<sub>4</sub> was increased progressively from 10 to 50 mM, the accumulated  $H_2O_2$  rose dramatically from 66.8 to 129.2 mg  $L^{-1}$ , while it only increased marginally to 141.1 mg  $L^{-1}$  for further increase to 100 mM. The increase in system performance associated with an increase in electrolyte concentration is due to a higher conductivity of the electrolyte resulting in a higher current (see Table S2 and Figure. S8) and enhanced mass transfer of O<sub>2</sub>, thereby facilitating the formation of  $H_2O_2$  [55,56]. Nevertheless, when the concentration of Na<sub>2</sub>SO<sub>4</sub> was increased from 50 to 100 mM, excessive Na<sub>2</sub>SO<sub>4</sub> precipitated on the electrode surface, leading to a decrease in active sites and a corresponding reduction in  $H_2O_2$  generation [57].

### 3.5. Electrochemical stability tests of 3D PyrC electrode for repeated electrosynthesis of $H_2O_2$

The evaluation of the durability of 3D PyrC electrode prepared based on additive manufacturing technology is essential for future potential applicability. Therefore, the performance for the microbial electrosynthesis of  $H_2O_2$  was assessed throughout 10 consecutive cycles of the MES employing this electrode. The experimental conditions were maintained according to the previously obtained optimal operating parameters, with the only modification being the replacement of the catholyte at the end of each cycle. As shown in Fig. 5a, the  $H_2O_2$  accumulated after each of the 10 consecutive cycles at the cathode remained nearly unaltered, with a concentration of around 130 mg L<sup>-1</sup>, indicating that the electrode was not deactivated. During this time, the system current remained constant at 6 mA for 10 cycles (Fig. 5b). The above findings suggest that the novel 3D PyrC electrode has excellent stability and reproducibility for the microbial electrochemical  $H_2O_2$  production.

### 3.6. Evaluation of scalability and mechanical properties of 3D PyrC electrodes

Due to the size limitation of the 3D printer used in this study, the largest 3D PyrC electrode that can be fabricated is 34 mm in length, 19 mm in width, and 5 mm in height, which is the original size we used in the aforementioned experiments with 9 mesh levels. Considering the adaptability of future applications and the potential requirements related to the scalability of the electrodes, additional research was conducted on the efficacy of electrodes with varying dimensions for in situ microbial electrosynthesis of H<sub>2</sub>O<sub>2</sub>. Thus, we prepared 3D PyrC electrodes with footprints half (0.5x) and twice (2x) the original size. Firstly, when observing the external structure of the smaller 3D PyrC electrode, it can be observed that shrinkage is also very uniform and isotropic, and the shape is well preserved. This is mainly attributed to the almost identical shrinkage ratio of the 3D printed electrode precursor structure during the pyrolysis process (Fig. 6a) [22]. For scalability, we investigated the performance of two 3D PyrC electrodes of the original size connected in series (Fig. 6a). First, electrochemical characterization including LSV and CV was conducted to study the electrochemical properties of the three types of 3D PyrC electrodes, indicating superior electrocatalytic ORR capability with increasing electrode size (Fig. S9). Most importantly, the application of electrodes with larger sizes also resulted in more H<sub>2</sub>O<sub>2</sub> generation (Fig. 6b). In particular, the accumulation of H<sub>2</sub>O<sub>2</sub> over 12 h was 67.3, 129.2, and 161.8 mg  $L^{-1}$  for 0.5x, original, and 2×3D PyrC electrodes, respectively. Indeed, larger electrodes had superior 2e<sup>-</sup> ORR electrocatalytic performance, attributed to a larger surface area and increased active sites, affirming the scalability of the 3D PyrC electrode. However, it is crucial to note that doubling the electrode size did not result in a proportionate increase in H<sub>2</sub>O<sub>2</sub> production compared to the original conditions. The relationship between electrode size and H2O2 production is not necessarily linear, and other factors such as mass transfer limitations and electrochemical reactions can significantly influence the overall efficiency and performance of the system. Further optimization of the reactor design and operational parameters for a given electrode size might be required to improve the output.

The 3D PyrC electrodes developed in this study exhibited



Fig. 5. Evaluation of the reusability of 3D PyrC electrode in a dual-chamber MES reactor. (a)  $\rm H_2O_2$  production and (b) recorded system current for 10 consecutive cycles.



Fig. 6. Evaluation of scalability of 3D PyrC electrodes. (a) 3D PyrC electrodes with different sizes, (b) variation of cathodic microbial electrosynthesis of  $H_2O_2$  versus time using 3D PyrC electrodes with different sizes.

commendable mechanical properties. In a specific experiment, we applied a load of 400 g to an electrode, exceeding its weight by approximately 12,000 times (refer to video S1). Remarkably, the electrode not only bore the load successfully but also showed no apparent signs of damage or cracking, underscoring its exceptional mechanical strength. Additionally, during several months of experimentation, the electrodes remained submerged in water without displaying any degradation or physical alterations, underscoring their outstanding durability and stability in aqueous environments.

### 3.7. Energy consumption and cost of 3D PyrC electrode

The main operational cost of MES for synthesizing H<sub>2</sub>O<sub>2</sub> in MEC mode is related to the electrical energy consumption of the process. Correspondingly, the calculated electrical energy consumption based on the above optimal conditions for 3D PyrC electrode, GDE, carbon cloth, carbon felt, and graphite were 1.02, 2.37, 3.75, 5.83, 7.01 kWh kg<sup>-</sup> H<sub>2</sub>O<sub>2</sub>, respectively (calculated based on the formula listed in Text S3). In addition, the energy consumption in previous studies employing MES for the synthesis of H<sub>2</sub>O<sub>2</sub> using different types of cathode electrodes was listed in Table S3. Overall, the energy consumption associated with 3D PvrC electrode is considerably lower than the one of conventional electrochemical setups for producing H<sub>2</sub>O<sub>2</sub> (ranging from 4.40 to 8.90 kWh kg<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>) [41] and MES that use conventional 2D electrodes (ranging from 2.37 to 7.01 kWh kg<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>). Furthermore, Table S3 also reveals that 3D graphite particle electrode composed of multiple PTFE-modified graphite particles with diameters of 2-3 mm prepared using non-3D printing technology [41], has exhibited a higher  $H_2O_2$ production rate (88.20 vs 10.77 mg  $L^{-1} h^{-1}$ ) in MEC mode compared to the 3D PyrC electrode used in this study. This can be attributed to the direct absorption of pumped oxygen by the porous structure of the electrode, facilitated by PTFE modification, instead of being dissolved in the catholyte, thereby overcoming the limitation of low H<sub>2</sub>O<sub>2</sub> production caused by low oxygen solubility [10]. However, it should be noted that the introduction of the PTFE catalytic layer increases costs and poses challenges related to long-term performance degradation. Besides, due to the excellent performance of larger-sized 3D PyrC electrode and their good scalability, it is anticipated that the energy consumption could be further reduced. There, our prior research has demonstrated that scaling up MES systems can obviously lower their energy consumption [6.39].

Based on our current lab-scale production method, the approximate cost of fabricating an electrode is around 4–5 Euros. This estimation includes the cost of materials and the electricity consumption required for the 3D printing and pyrolysis process. However, it is important to note that this cost estimate is based on our current lab-scale production setup, which involves manual processes and small batch sizes. If we were to transition to mass production using more efficient and automated techniques, we could expect to reduce the cost of the electrodes significantly. Overall, the electrode fabrication process we have developed holds promise for producing high-performance electrodes at an affordable cost. We are confident that further optimization of our manufacturing methods will further reduce the cost and enable commercialization of our technology.

### 3.8. Feasibility and applicability in a BEF process for the efficient removal of micropollutants

As discussed above, the 3D PyrC electrodes in the MES perform optimally for the production of high concentrations of  $H_2O_2$  at an acidic pH (e.g., pH 2), which is precisely the optimal pH range for the Fenton process[58]. Therefore, we further evaluated this novel electrode in BEF process to explore its applicability as a tertiary treatment technology for efficiently removing refractory micropollutants from WWTPs' secondary effluent. Consequently, tests on removing 24 typical micropollutants spiked in real WWTPs secondary effluent (Lyngby WWTP, Copenhagen,

Denmark) were conducted. The characteristics of this WWTPs secondary effluent are shown in Table S1. Since the real WWTPs secondary effluent has a specific level of conductivity and adding Na<sub>2</sub>SO<sub>4</sub> as an electrolyte would raise costs and necessitate desalinating before discharging, no additional electrolyte was used in this experiment. The BEF operational parameters comprised pH of 2, aeration velocity of 0.02 mL min<sup>-1</sup> mL<sup>-1</sup>, Fe<sup>2+</sup> of 0.2 mM, and applied voltage of 0.4 V. As can be seen in Fig. 7, the removal rates of the selected 24 typical micropollutants varied significantly, but all were eradicated entirely within 4 h and the removal was compatible with first-order kinetics. In particular, half of these micropollutants (bezafibrate, carbamazepine, clofibric acid, diclofenac, hydrochlorothiazide, iohexol, metoprolol, mycophenolic acid, sertraline and venlafaxine) were even removed in one hour or less, owing to the strong oxidizing capability of the hydroxyl radicals (OH) generated through Eq. (15).

Remarkably, the BEF process with the 3D PyrC electrode outperformed the traditional BEF process with the graphite electrode regarding micropollutants removal [7,40,49]. This was mainly due to the high H<sub>2</sub>O<sub>2</sub> yield and the greater iron regeneration capacity (Eq. (16)), which was attributed to the increased surface area and number of active sites. Additionally, compared to graphite electrode with 2D surfaces, the BEF with 3D PyrC electrode had superior anodic COD removal capacity (89% vs. 30% in 12 h, see Fig. S10a) due to the higher current (Fig. S10b) accelerating the metabolization of organic matter by the microorganisms at the anode [13].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^-$$
(15)

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \to \mathrm{Fe}^{2+} \tag{16}$$

These observations indicated that the 3D PyrC electrode fabricated based on additive manufacturing technology provided an appealing platform for microbial electrosynthesis of  $H_2O_2$  and simultaneous wastewater treatment.

### 3.9. Toxicity test

Ecotoxicity experiments were performed on the effluent after micropollutants removal employing Vibrio fischeri to determine the safety of the BEF technology using the 3D PyrC electrode as a tertiary treatment process. The duration of sample treatment was identical to the



**Fig. 7.** Pseudo-first-order rate constants (k) of the degradation of 24 typical micropollutants from WWTP secondary effluent during BEF treatment using 3D PyrC electrode and graphite, respectively.

one in the BEF experiment above. Fig. 8 displays the percentage of bioluminescence inhibition of the samples against Vibrio fischeri after 10 and 20 min of exposure. Inhibition levels below 20% are typically regarded as lacking serious adverse consequences [39]. It can be seen that the inhibition rates of the original sample after 10 and 20 min of exposure were as high as 55% and 71%, respectively, which was due to the addition of up to 24 micropollutants, including antibiotics (Azi-thromycin and Clarithromycin). The results indicate the presence of certain biological toxicity. Satisfactorily, the inhibition rate of all samples was lower than 20% after 3 h and lower than 10% after 4 h, indicating no significant remaining biological toxicity in the effluent. Thus, it can be inferred that micropollutants were swiftly detoxified in the BEF process equipped with the 3D PyrC electrode, providing a safe and ecologically friendly technique for tertiary wastewater treatment.

### 4. Conclusions

In this study, we demonstrated a facile method for fabricating highly structured 3D PyrC electrodes using an additive manufacturing technique followed by pyrolysis. Subsequently, we investigated the electrodes in a MES reactor to boost H<sub>2</sub>O<sub>2</sub> synthesis. The novel 3D PyrC electrode outperformed conventional carbon electrodes (e.g., graphite, carbon felt, carbon cloth, and GDE) in anodic COD removal and cathodic H<sub>2</sub>O<sub>2</sub> production due to high and accessible electrode surface area in the 3D mesh. The results suggest that this electrode can accumulate approximately 130 mg  $L^{-1}$  of  $H_2O_2$  in 12 h under optimum conditions and provide current efficiencies above 60% even in repetitive cycles. As a consequence of the highly efficient H<sub>2</sub>O<sub>2</sub> microbial electrosynthesis at the 3D PvrC electrode, the removal efficiency of 24 selected typical micropollutants in the subsequent BEF process was enhanced. Given this promising electrode manufacturing technology, 3D PyrC electrodes with a large specific surface area, architected porous microstructure with mesh sizes below 100 µm and excellent structural homogeneity can provide numerous active sites, greatly enhance the O2 transfer and increase H<sub>2</sub>O<sub>2</sub> production. In contrast to conventional methods, there is no need for costly modifications and sophisticated reaction units to improve the electrode performance, making it more affordable. Additionally, the scalability, reusability, and mechanical characteristics of the 3D PyrC electrode were commendable, underscoring its pragmatic suitability for large-scale applications. This revolutionary method holds the potential to facilitate sustainable and cost-effective H<sub>2</sub>O<sub>2</sub> synthesis, opening avenues for the large-scale implementation of the BEF process.

### **Environmental implication**

Hydrogen peroxide (H2O2) is an environmentally friendly oxidant gaining popularity in various applications, especially for environmental remediation. Our research shows a novel electrode design for efficient sustainable microbial electrosynthesis of H2O2 and subsequent environmental remediation by incorporating cutting-edge additive manufacturing technology, microbial electrochemistry, and the Fenton process. Refractory micropollutants in wastewater can negatively impact ecosystems and human health.

### CRediT authorship contribution statement

**Rezaei Babak:** Formal analysis, Methodology, Resources, Writing – review & editing. **Keller Stephan Sylvest:** Funding acquisition, Methodology, Resources, Supervision, Writing – review & editing. **Zou Rusen:** Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Zhang Yifeng:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.



Fig. 8. Toxicity assessment at two assay times 10 min and 20 min in terms of inhibition percentage of *Vibrio Fischeri* for the BEF treated effluent.

#### **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.

### Data Availability

Data will be made available on request.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.133681.

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