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Fabrication of a permeable SnO$_2$-Sb reactive anodic filter for high-efficiency electrochemical oxidation of antibiotics in wastewater

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A B S T R A C T

Electrochemical oxidation (ECO) is an appealing technology for treating emerging organic pollutants in wastewater. However, the conventional flow-by ECO process is expensive with a low energy efficiency owing to the limitations of mass transport of contaminants to the limited surface area of the anode. In this study, a novel permeable SnO$_2$-Sb anode was fabricated by one-step sintering using micrometer-sized (NH$_4$)$_2$CO$_3$ grains as the pore-forming agents. This permeable anode without Ti substrate functioned as a reactive anodic filter (RAF) in an ECO cell to treat wastewater containing ciprofloxacin (CIP). Forcing the wastewater through the porous RAF depth-wise improved the mass transport and vastly enlarged the electroactive surface area. Compared with the conventional flow-by configuration, the flow-through RAF exhibited a 12-fold increase in the mass transfer rate constant ($60.7 \times 10^{-6}$ m s$^{-1}$) and a 5-fold increase in the CIP degradation rate constant (0.077 min$^{-1}$). At a cell potential of 4.0 V, more than 92% of the CIP was degraded in a single-pass operation at a filtration flux of 54 L m$^{-2}$ h$^{-1}$ and a short retention time of 1.7 min through the RAF. The robustness and stability of the RAF were demonstrated by its remarkable CIP degradation efficacy of 99% during 200 h of operation. The mechanism of CIP degradation was examined using probe molecules and density functional theory calculations and found to be a combined effect of direct electron transfer and oxidation by generated radicals ($\text{OH} \text{ and } \text{SO}_4^{2-}$). The great potential of RAF in flow-through ECO was further validated by its effective removal ($>92%$) of various organic pollutants in actual municipal wastewater at a low energy consumption of 0.33 kWh m$^{-3}$. The RAF-based ECO process thus provides an advanced environmental technology for the oxidation of toxic and recalcitrant organic pollutants in wastewater.

1. Introduction

The increasing presence of emerging organic pollutants in wastewater is posing serious risks to human health and ecosystems. Among the pollutants, antibiotics have caused growing concerns due to their adverse effects on ecosystems and the increasing threat of antimicrobial resistant bacteria (Liu et al., 2015). Many of these pollutants are toxic and resistant to conventional biological wastewater treatment (Kümerer, 2019). There is a pressing need to develop more efficient technologies for treating toxic and recalcitrant organic pollutants in wastewater. The electrochemical oxidation (ECO) process is an appealing and effective technology for wastewater treatment, given its strong oxidation capacity, simple operation, environmental compatibility, and chemical-free processing (Moreira et al., 2017; García-Segura et al. 2020). In essence, ECO is a heterogeneous catalysis reaction, in which the degradation of the contaminants (R) mainly occurs at the anode–liquid interface through both direct oxidation (R1) and indirect reaction with radicals (such as ‘OH) generated by the anode (R2) (Martínez-Huitle and Ferro, 2006). Therefore, the effectiveness of ECO treatment largely depends on the properties of the anode materials and the interfacial area (Radjenovic and Sedlak, 2015). Several anode materials, such as PbO$_2$ (Feng and Li, 2003; Yang et al., 2021), doped SnO$_2$ (Li et al., 2005; Cui et al. 2009), TiO$_2$ (Ganiyu et al., 2016), and boron-doped diamond (BDD) (Sires and Brillar, 2012), exhibit reactive capability for catalytic ECO of organic pollutants. Despite the development of anode materials, the practical use of ECO has been hindered by the high cost and low energy efficiency of the process, owing mainly to the limitations associated with the mass transport of the organic pollutants...
from the bulk solution to the limited surface area of the anode (Chaplin, 2018).

\[ R \rightarrow [R]^+ + e^- \]  \hspace{1cm} (R1)

\[ H_2O \rightarrow OH^- + H^+ + e^- \]  \hspace{1cm} (R2)

Currently, most anodes are implemented in the form of conventional 2D electrode plates and operated in batch configuration or flow-by configuration. In these configurations, which entail a large hydrodynamic diffuse boundary layer (~100 μm) on the anode surface, the diffusion of pollutants from the bulk solution to the anode is the limiting step (Chen et al., 2020). To overcome these limitations, the flow-through configuration, in which wastewater is forced through a porous anode depth-wise, has been proposed for the ECO process (Shi et al., 2019). Flowing through the porous anode decreases the diffusional distance of the reactants to a length scale on the order of the pore radius (<1 μm) of the anode, thus significantly improving the mass transport (Zaky and Chaplin, 2013). In addition, the flow-through configuration provides a much larger electroactive surface area as it uses the interior area of the RAF instead of only the exterior surface area. This porous and permeable anode, which simultaneously functions as a filter, significantly improves the degradation of the recalcitrant pollutants and hence contributes to the development of a highly effective ECO technology for the decentralized wastewater treatment (Liu et al., 2020; Ganzenko et al., 2021).

An anode that is both permeable and reactive is essential to the flow-through ECO treatment system. Although state-of-the-art BDD film anodes exhibit activity toward both reactions R(1) and R(2), the high cost and difficulty of forming a porous structure have limited their practicability (Chaplin, 2013). Research has mainly focused on the porous materials for making permeable electrodes, such as carbon nanotubes and TiO₂ (Vecitis et al., 2011; Zaky and Chaplin, 2013). However, pristine carbon nanotubes are not effective for anodic oxidation because of their ‘OH generation inactivity, while TiO₂ is unsatisfactory with respect to both stability and ‘OH generation capability (Gayen et al., 2018). From a techno-economic perspective, doped SnO₂ is a highly attractive anode material for ECO, given its high activity toward both reactions R(1) and R(2), low cost, and high stability (Cui et al., 2009; Martinez-Huitie and Brillas, 2009; Yu et al., 2019). Besides, compared with the rigorous conditions for fabricating porous TiO₂ anodes (high temperature in H₂ atmosphere), the doped SnO₂ anodes can be made in air atmosphere at a lower temperature, which is easy to scale up. A freestanding porous SnO₂ anode with a high reactivity and long service life was recently reported for the ECO treatment of organic wastewater in batch operation, which would overcome the challenges of the current Ti substrate-based SnO₂ anodes (Mora-Gomez et al., 2018; Drouguet et al., 2020; Mora-Gomez et al., 2020). However, a support-free 3D porous SnO₂ anode as a reactive filter with high reactivity and permeability for ECO wastewater treatment is yet to be fabricated, partly due to the poor sinterability of SnO₂ and the challenges in fabricating porous structures (Nisiro et al., 2003).

In this study, a novel freestanding and permeable SnO₂-Sb anode was fabricated by an innovative one-step compressing and sintering technique for ECO treatment. The anode was operated as a reactive anodic filter (RAF) in the single-pass flow-through process for the degradation and removal of organic pollutants in wastewater. The RAF electrode was fabricated using a novel one-step sintering technique, and (NH₄)₂CO₃ grains were used as the pore-forming agent to tailor the pore structure of the anode. Compared with the conventional flow-by operation, the RAF-based flow-through ECO process demonstrated exceptional performance in the oxidation of ciprofloxacin (CIP), an antibiotic commonly found in wastewater. The RAF electrode was characterized, and the enhancement in the mass transport was demonstrated experimentally. Tests involving specific probe molecules and density functional theory (DFT) calculations revealed the key mechanism underlying the ECO treatment of CIP. The robustness, feasibility, and stability of the RAF-based ECO system were further evaluated with a durability test lasting over 200 h, antibiopic activity assessment of the wastewater samples, and degradation of various pollutants in actual wastewater.

2. Materials and methods

2.1. Chemicals and reagents

Antimynt tin oxide (SnO₂/Sb₂O₃, Sn:Sb = 9:1), potassium ferrocyanide (K₃Fe(CN)₆), potassium ferricyanide (K₃Fe(CN)₆), ammonium carbonate ((NH₄)₂CO₃), and moxifloxacin (MOX) were obtained from Aladdin. CIP, oxalic acid (OA), coumarine (COU), paraffin oil, and sodium sulfate (Na₂SO₄) were purchased from Sigma-Aldrich. Other chemicals and solvents were purchased from Merck. Deionized (DI) water (18.2 MΩ cm; Milli-Q) was used for the laboratory tests. Municipal wastewater (secondary effluent after treatment) was collected from Stanley Sewage Treatment Works (Stanley STW) in Hong Kong.

2.2. Preparation of the permeable anode as the RAF

The porous and permeable 3D SnO₂-Sb anode was fabricated using a one-step sintering method. Specifically, 6.0 g of the SnO₂/Sb₂O₃ powder (~100 nm) was thoroughly mixed with 3.0 g of (NH₄)₂CO₃ grains (~100 μm) for 10 min to make a uniform blended mixture. Several drops (0.6 g) of paraffin oil were added to the blended powder and mixed for 10 min. This mixture was placed into a circular die 4.0 cm in diameter. Using a hydraulic press (HF-Keijing, China), a uniaxial pressure of approximately 200 bar was applied on the mixture to form a compressed disc, the precursor of the anode. Finally, the precursor disc was sintered in a muffle furnace at 800 °C in air for 6 h to produce a freestanding SnO₂-Sb anode. During sintering, the (NH₄)₂CO₃ grains decomposed and vaporized, creating a porous structure with micrometer-sized pores and channels. This structure, made in two thicknesses (2 and 4 mm), served as the RAF for wastewater treatment.

2.3. Material characterization

The crystalline phases of the SnO₂-Sb anodes were identified by X-ray diffraction (XRD, Bruker D8 Advance). The morphologies of the materials were examined by scanning electron microscopy (SEM; S-4800, Hitachi) and scanning transmission electron microscopy (STEM; Tecnai G220 S-Twin, FEI). The porosimetry of the anodes was characterized using a Hg porosimeter (PoreMaster GT-60, Quantachrome).

2.4. ECO treatment tests

An electrolysis cell (4 cm in diameter, 2 cm in length) with the as-prepared RAF as the anode and Ti mesh as the cathode was used in the ECO wastewater treatment tests (Fig. 1a). The tests were conducted in the single-pass continuous-flow mode by pumping wastewater through the ECO cell without recirculation. In the commonly used conventional flow-by configuration (Fig. 1b), the antibiotic wastewater was flowed between the anode and cathode plates in the ECO cell, with no water flow across the anode. In most tests, as shown in Fig. 1c, the flow-through configuration was operated, in which the antibiotic wastewater was forced through the anode depth-wise.

The antibiotic wastewater contained 10 μM CIP, a typical antibiotic contaminant (Li et al., 2020), and 0.1 M Na₂SO₄ as the supporting electrolyte. This model antibiotic wastewater was pumped through the Ti mesh cathode and then the RAF in the ECO cell using a peristaltic pump (BT100-2 J, Longer Pump) at a pre-determined flow rate between 0.5 and 2 mL min⁻¹, which corresponded to an overall treatment time (or hydraulic retention time, HRT) between 48 and 12 min. The resulting filtration flux of the RAF electrode ranged between 27 and 108 L m⁻² h⁻¹ (LMH), which corresponded to an apparent retention time between 3.4 and 0.85 min. A constant cell potential (0–5.0 V) was
applied between the anode and cathode using an electrochemical workstation (PARSTAT MC 1000, Princeton Applied Research). To evaluate the CIP degradation performance, and the treated water from the outlet was sampled at pre-determined time intervals. The solution inside the ECO cell was also sampled for analysis before it flowed through the RAF.

In addition to the antibiotic wastewater containing 10 μM CIP, solutions of OA (1 mM) and COU (1 mM) were used as probe organic molecules to investigate the \( \bullet \text{OH} \) generation and direct oxidation in the RAF-based ECO process. The ECO tests were conducted at a RAF flux of 54 LMH and cell potentials of 0 – 4 V.

2.5. Determination of the mass transfer rate constant

The mass transfer rate constant \( (k_m) \) in the porous RAF electrode was determined using the limiting current technique (Canizares et al., 2006) as follows:

\[
k_m = \frac{I_{\text{lim}}}{nFAC}
\]

where \( I_{\text{lim}} \) is the limiting current, \( n \) the number of electrons transferred \( (n = 1) \), \( F \) the Faraday constant \( (96,485 \text{ C mol}^{-1}) \), \( A \) the anode surface area \( (\text{m}^2) \), and \( C \) the bulk concentration of \( \text{Fe(CN)}_6^{4-} \) \( (\text{mol m}^{-3}) \) used in the \( k_m \) determination tests. Additional details of the test are described in Text S1, Supporting Information.

2.6. Analytical methods

The concentrations of CIP, MOX, and COU in the water samples were measured by a high-performance liquid chromatography (HPLC, e2695, Waters) system using a UV–vis photodiode array detector and a C18 column \( (250 \text{ mm} \times 4.6 \text{ mm} \times 5 \text{ μm}) \) at 35 °C. The mobile phase composed of methanol/H₂O containing 0.1% \( \text{H}_3\text{PO}_4 \) \( (75:25, \text{ v/v}) \) was supplied at 1.0 mL min \(^{-1} \) for the CIP and MOX detection, and the mobile phase for COU detection was the methanol/H₂O \( (50:50, \text{ v/v}) \) mixture with a flow rate of 1.0 mL min \(^{-1} \). The detection wavelength was set at 270 nm for CIP, 295 nm for MOX, and 277 nm for COU. OA was quantified by HPLC using a BP-OA organic acid column \( (300 \text{ mm} \times 7.8 \text{ mm} \times 5 \text{ μm}) \). The concentrations of methylene blue (MB) and rhodamine B (RhB) were determined using a UV–vis spectrophotometer (Libra S12, Biochrom) at wavelengths of 644 and 554 nm, respectively. The presence of persulfate \( (\text{S}_2\text{O}_8^{2-}) \) in the water was detected according to the ISCO method (see Text S2, Supporting Information for details) (Liang et al., 2008). The energy consumed to degrade CIP was estimated as the electrical energy per order \( (E_{\text{EO}}; \text{kWh g}^{-1}) \) (Gayen et al., 2018), which is defined as follows:

\[
E_{\text{EO}} = \frac{E_{\text{cell}}I_{1000}q_m\log(C_0/C_t)}{1000}
\]

where \( E_{\text{cell}} \) is the cell potential \( (\text{V}) \), \( I \) the current \( (\text{A}) \), \( q_m \) the mass flow rate of the contaminant \( (\text{g h}^{-1}) \), and \( C_0 \) and \( C_t \) the initial and final CIP concentrations \( (\text{mg L}^{-1}) \), respectively.

3. Results and discussion

The schematic of the electrochemical treatment system equipped with the SnO₂–Sb RAF electrode is shown in Fig. 1a. The porous and permeable 3D RAF, the core component of the ECO system, allows wastewater to flow depth-wise through the anode, thus providing a multitude of active sites for direct organic oxidation and reactive radical generation. Moreover, the RAF-based ECO configuration implemented in this study effectively overcomes the mass transport limitation, thereby realizing the high-rate and high-efficiency degradation of organic contaminants in a single-pass operation.

3.1. Preparation and characterizations of RAF for ECO treatment

Because the RAF is implemented in the flow-through configuration, the ideal RAF electrode is of a porous and permeable structure with
micrometer-sized internal pores and channels. Therefore, freestanding SnO$_2$-Sb RAF anodes of diameter 40.0 mm and thickness 4.0 mm (Fig. 2a) were fabricated without the supporting Ti substrate, and the 3D porous anode was fabricated by simple one-step sintering of the compressed precursor of SnO$_2$/Sb$_2$O$_3$ with (NH$_4$)$_2$CO$_3$ grains as the pore-forming agent. The pore structure of the RAF electrode can be modified by varying the amount and size of the (NH$_4$)$_2$CO$_3$ grains.

The SEM image of the anode surface (Fig. 2b) shows uniform pores and channels of diameter approximately 0.5 μm between the SnO$_2$-Sb clusters. The TEM image (Fig. 2c) indicates that the SnO$_2$-Sb particles sintered together to form a monolithic structure, imparting the anode plate with sufficient mechanical strength. Further characterization by Hg intrusion porosimetry revealed that the RAF electrode has a hierarchical porous structure with a bimodal pore size distribution, the two dominant pore sizes being small pores < 0.2 μm and large pores > 10 μm in diameter (Fig. 2d). The interconnected large pores facilitate water permeation through the RAF and enhance water and chemical transport to the active sites inside the anode. The specific surface area of the anode material is 19.6 m$^2$ g$^{-1}$ and is mainly contributed by the small pores (Fig. 2e). The porosimetry analysis revealed a remarkable porosity of 76.4%, substantially higher than that reported for the porous Ti$_2$O$_3$ anode (30.7%) (Zaky and Chaplin, 2013). The electroactive surface area of the porous anode was determined by electrochemical impedance spectroscopy (EIS) to be 0.62 m$^2$ cm$^{-2}$ (see Text S3, Supporting Information, for the details) (Zaky and Chaplin, 2013). This large electroactive surface area (relative to the geometric surface area) provides numerous active sites for the direct oxidation and radical generation during the ECO process. Moreover, the XRD patterns of the RAF electrode in Fig. 2f, which show the sharpness and intensity of its diffractions before and after the ECO treatment tests, indicate the high crystallinity and stability of the anode material. The RAF shows hydrophilic property, with a contact angle value of 13.4°. The water permeability of the porous anode was determined to be 527 LMH bar$^{-1}$ (Fig. S1), suggesting that the RAF can be classified as a microfiltration membrane filter.

### 3.2. CIP degradation by ECO treatment

CIP was used as a model antibiotic contaminant to evaluate the effectiveness of the ECO system for the degradation of toxics and recalcitrant emerging organic pollutants in wastewater treatment. The SnO$_2$-Sb anode was tested in the flow-by and flow-through configurations (Fig. 3a) without recirculation. The CIP wastewater was pumped at 1 mL min$^{-1}$ into the ECO cell, resulting in an HRT of 24 min for the ECO treatment and a filtration flux of 54 LMH through the RAF in the flow-through configuration. In the open circuit potential (OCF, 0.41 V) condition without the DC input, a small reduction in CIP was found, indicating little adsorption by the anode. In the conventional flow-by configuration with a DC of 4.0 V, the ECO treatment removed approximately 48.0% of the CIP. In the flow-through configuration with the RAF (cell potential of 4.0 V, anode potential of 2.9 V vs. RHE), the CIP removal efficiency increased significantly to 92.1% under the same HRT condition as the flow-by configuration.

Further insight into the ECO treatment performance was obtained by assessing the related rate constant ($k_{obs}$) with the pseudo-first-order model in Fig. S2 and energy consumption ($E_{EO}$) (Fig. 3b). In the same OEC cell, the $k_{obs}$ of CIP degradation for the flow-through anode (0.077 min$^{-1}$) was more than five times that of the flow-by anode (0.014 min$^{-1}$). The $E_{EO}$ of CIP degradation for the flow-through mode was 0.31 kWh g$^{-1}$ CIP, significantly lower than that for the flow-by mode (2.43 kWh g$^{-1}$ CIP). These results prove the superiority of the permeable RAF in the ECO treatment of emerging and toxic organic contaminants within a short period of only 1.7 min through the RAF. In contrast to the flow-by configuration, flow through the RAF electrode greatly enhanced the transport of water and contaminants to the multitude of electroactive sites inside the porous anode. Moreover, the organic contaminants were confined close to the surface of the electrocatalytic materials inside the RAF. The improved mass transport and ECO reaction configuration of the RAF-based system facilitated the direct oxidation and reactive radical generation for organic degradation, resulting in excellent treatment performance.

To further elucidate the ECO reaction kinetics in the RAF-based system, the CIP wastewater treatment process was divided into two stages: (I) CIP degradation in the bulk solution between the cathode and anode, followed by (II) CIP degradation in the interior flow through the RAF plate. As shown in Fig. 3c, CIP in wastewater ($C_0$) first passed the Stage I region in the ECO cell with a long retention time ($\theta_1$) and a decreased concentration ($C_{\theta_1}$) before flowing through the thickness of the RAF (Stage II region) with a short retention time ($\theta_2$). The concentration of CIP in the solution in the Stage I region was analyzed (Fig. S3, Supporting Information), and the relative contributions ($f$) of the Stage I and II regions to the overall CIP degradation were calculated (Eqs. (3) and (4); compared in Fig. 3d). In the ECO process with a RA filtration flux of 54 LMH, CIP degradation by the permeable anode with a short retention time of less than 2 min in RAF (i.e., Stage II) accounted for 75.0% of the observed CIP removal. This result affirms that the organic contaminant

![Fig. 2. Characterizations of the RAF: (a) photograph showing two RAF plates, (b) SEM image and (c) TEM image of the RAF material, (d) and (e) Hg intrusion porosimetry analysis of the pore size distribution, and (f) XRD patterns of the RAF before and after the ECO wastewater treatment test.](image-url)
was more effectively degraded in the interior flow through the RAF than did in the bulk solution of the ECO cell.

\[ f_1 = \frac{C_0 - C_b}{C_0} \times 100\% \quad (3) \]

\[ f_2 = \frac{C_b - C_e}{C_0} \times 100\% \quad (4) \]

The permeable and reactive anode can be considered a plug-flow reactor, for which the reaction rate constant \( k \) (min\(^{-1}\)) can be calculated from the following first-order reaction kinetic equation (Fogler, 2016):

\[ \ln\left(\frac{C_e}{C_b}\right) = k \theta \quad (5) \]

The pseudo-first-order rate constant for the Stage II region (\( k_2 = 1.34 \text{ min}^{-1} \)) was approximately 130 times higher than that for the bulk solution in the ECO cell (\( k_1 = 0.01 \text{ min}^{-1} \)), mainly due to the large electroactive surface area for direct oxidation/radical generation and enhanced mass transport in the interior pores of the RAF.

It can therefore be asserted that the thicker the RAF, the higher the organic degradation efficacy. To verify this hypothesis, the degradation of CIP (25 mg L\(^{-1}\)) by 2- and 4-mm-thick RAFs was comparatively evaluated (Fig. S4, Supporting Information). In stable operation, the thicker RAF exhibited a higher CIP degradation removal (82%) than did the thinner RAF (65%). Thus, the treatment capacity and performance of the RAF-based ECO system can be partially controlled by the thickness of the RAF. A thinner RAF permits a higher wastewater treatment flux with a lower organic removal efficacy, and a thicker RAF allows a lower flux for a higher removal efficiency. The ultra-high capability and excellent performance of the flow-through RAF in ECO treatment of organic pollutants were further demonstrated in Fig. 4. For initial CIP concentrations below 40 \( \mu \text{M} \), the RAF degraded ~ 90% of the CIP at a filtration flux of 54 LMH and a retention time \( \theta_2 = 1.7 \text{ min} \). When the filtration flux was decreased to 27 LMH, 100% of the CIP was removed.

![Fig. 3. ECO experiments in the flow-by and flow-through configurations: (a) CIP degradation, (b) pseudo-first-order degradation rate constants and energy consumption, (c) CIP degradation through the two flow-through stages of the RAF-based ECO cell, and (d) the relative contributions of the two stages to the overall CIP degradation (conditions: [CIP] = 10 \( \mu \text{M} \), [Na\(_2\)SO\(_4\)] = 0.1 M, cell potential = 4.0 V, pH = 6.0, RAF flux = 54 LMH, overall HRT = 24 min).](image)

![Fig. 4. Effects of (a) the influent concentrations and (b) flux on the RAF-based ECO treatment (conditions: [Na\(_2\)SO\(_4\)] = 0.1 M, cell potential = 4.0 V, pH = 6.0, flux = 54 LMH for (a), [CIP] = 10 \( \mu \text{M} \) for (b)).](image)
3.3. Mass transport and contaminant removal capacity

To further investigate the effect of mass transport on the organic degradation during ECO treatment, the mass transfer rate constant \( (k_m) \) was determined using the limiting current technique in the \( K_4Fe(CN)_{6}^{3-} \) oxidation test. Increasing the filtration flux (from 18 to 108 LMH) increased the apparent mass transfer rate constant from \( 5 \times 10^{-6} \) to \( 30 \times 10^{-5} \) m s\(^{-1}\), as evident in Fig. 5a, which shows a linear relationship between \( k_m \) and \( J \) \( (R^2 = 0.94) \). This linear relationship indicates that the increased flux through the RAF enhanced the mass transport of the reactants, which at a high flux is attributable to the micro-turbulence of the flow within the porous anode. Furthermore, for the ECO cell with a treatment flow rate of 2 mL min\(^{-1}\), \( k_m \) in the flow-through RAF configuration \( (60.7 \times 10^{-6} \text{ m s}^{-1}) \) was approximately 12-fold that in the flow-by configuration \( (5.0 \times 10^{-5} \text{ m s}^{-1}) \). The confinement of the contaminants in close proximity to the anode material inside the RAF electrode effectively reduced the mass transport limitation compared to the case in the flow-by ECO system.

The relationship between the CIP removal capacity and the mass transfer rate constant \( (k_m) \) at the different fluxes through the RAF was further analyzed. As shown in Fig. 5b, a linear correlation was found between the CIP removal capacity and \( k_m \) \( (R^2 = 0.99) \). The enhanced mass transport facilitated the rapid transport of contaminants to the active sites inside the porous RAF, thereby increasing the rate and capacity of organic degradation by the ECO treatment. But the pressure drop through the RAF increased with an increasing filtration flux. Nevertheless, the RAF-based ECO system performed well at filtration fluxes of up to 108 LMH and a short treatment time \(<1\text{ min}\) through the RAF. In summary, the porosity of the RAF allowed interior flow areas and enhanced the mass transport, thus substantially improving the organic degradation efficiency and capacity of the ECO process.

3.4. Mechanism of ECO by the RAF

The organic degradation performance of the RAF-based ECO cell was investigated at different applied cell potentials \((0-5.0 \text{ V})\) under the continuous single-pass mode. At a flow rate of 1 mL min\(^{-1}\) \((\text{Fig. 6a})\), the CIP removal efficiency first increased as the cell potential increased from 0 to 4 V and then decreased as the cell potential increased further to 5.0 V. High potentials \((>4.0 \text{ V})\) enhance \( O_2 \) generation at the porous anode, leading to considerable power loss and reduced current efficiency for CIP degradation. Moreover, the increased generation of \( O_2 \) bubbles at cell potentials of 5.0 V or higher clogs some of the pores and hence restricts the transport of organic contaminants to the electroactive sites of the RAF \((\text{Trellu et al., 2018})\).

Further insights into the ECO mechanism of the flow-through RAF were obtained experimentally using model organic probe molecules. OA was used as the probe for direct electro-oxidation owing to its very low reactivity with ‘OH free radicals \((1.4 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1})\) \((\text{Ferro et al., 2010})\). The direct oxidation of OA on the surface of the anode material can be expressed as follows:

\[
C_2H_5O_2^- + 2Fe^{3+} \rightarrow O_2 + 2C_2H_5O_2^+ + 2e^- 
\]

(R3)

The oxidation of OA \((1 \text{ mM})\) by the RAF-based ECO cell was tested at potentials of \(0-4.0 \text{ V}\) and a filtration flux of 54 LMH \((4.86 \text{ g m}^{-2} \text{h}^{-1})\). The adsorption effect can be neglected considering the slight decrease of OA concentration at 0 V \((\text{Fig. 6b})\). With increases in the cell potential from 2.0 to 4.0 V, the OA degradation efficiency improved from 57.5% to 99.0%. Higher cell potentials greatly improved the oxidation potential, leading to rapid direct OA oxidation.

COU was used as an effective ‘OH probe due to its resistance to direct oxidation and its rapid reaction with ‘OH radicals \((\text{Bejan et al., 2012})\). At a cell potential of 4.0 V \((\text{anode potential of 2.9 V vs. RHE})\), nearly all of the COU was degraded by the flow-through RAF \((\text{Fig. 6c})\), indicating the oxidation of COU by ‘OH radicals within the porous RAF. However, at a cell potential of 3.0 V \((\text{anode potential of 1.9 V vs. RHE})\) \((\text{and lower})\), the COU removal efficiency decreased considerably to 40% \((\text{and lower})\), apparently because ‘OH generation requires a high oxidation potential \((E^0 = +2.74 \text{ V vs. SHE})\). The foregoing COU and OA probe test results affirm that the RAF provides a large number of electroactive sites for direct oxidation and ‘OH generation during flow-through ECO operation at 4.0 V. The observed rapid organic degradation is due to the synergistic effect of direct electron transfer at the SnO\(_2\)-Sb surface and oxidation by the radicals.

For an in-depth understanding of the CIP degradation mechanism, the direct CIP oxidation was comprehensively investigated through DFT calculations using the B3LYP functional \((\text{detailed in Text S4, Supporting Information})\). For the optimized structures of CIP and its oxidation products \((\text{Fig. S5})\), Fig. 6d presents the enthalpy of activation \((\Delta H)\) as a function of the anodic potential \((\text{calculated using Eq. (3)})\) \((\Delta H (75.4 \text{ kJ mol}^{-1})\) and \( E^0 (0.77 \text{ V vs. SHE}) \) were calculated from the DFT results. As shown in Fig. 6d, direct CIP oxidation occurred without any obvious activation barrier when the anodic potential reached 1.54 V vs. SHE, much lower than the threshold for ‘OH generation \((2.74 \text{ V vs. SHE})\). Thus, consistent with the experimental observations, at a low but appropriate potential, the direct oxidation of CIP is more likely to occur than its oxidation by ‘OH radicals. At an increased potential, the intermediate radical species \((\text{CIP}^-)\) is highly reactive with ‘OH generated \((\text{Gayen et al., 2018})\), facilitating ultrafast CIP degradation rate in the flow-through RAF.

Fig. 7 illustrates the mechanism of CIP degradation by the RAF, as identified through the experimental results and DFT calculations. When the CIP water flowed through the 3D permeable and reactive anode under the apparent action of advection-controlled transport, CIP, the model organic contaminant, was confined in close proximity to the
interior surface of the porous anode and was readily degraded by both direct electron transfer and strong oxidants such as \( \cdot \)OH radicals. This coexistence of direct oxidation and \( \cdot \)OH reactions was confirmed by the test results obtained using the probe molecules and by the values of activation energies based on DFT calculations. Furthermore, reactive sulfate species, namely \( \text{SO}_4^{2-} \) and \( \text{S}_2\text{O}_8^{2-} \), were detected in the RAF-based ECO system under the conditions of \([\text{Na}_2\text{SO}_4]=0.1 \text{ M}, \text{cell potential}=4.0 \text{ V}, \text{pH}=6.0, \text{flux}=54 \text{ LMH}, \) overall HRT = 24 min; (d) enthalpy of activation (\( \Delta H \)) as a function of anodic potential for CIP oxidation, determined by DFT using B3LYP functional.

The contributions of reactive radicals (‘OH and \( \cdot \)SO\(_4\)^{2-} \)) and direct oxidation to the degradation of organics in the RAF-based ECO system were evaluated by the quenching tests using methanol as both the ‘OH and \( \cdot \)SO\(_4\)^{2-} scavenger (Li et al., 2018). CIP removal was decreased by approximately 45% after adding excess methanol (2 M) in the solution (Fig. S6). The quenching test results indicated that, in addition to the direct oxidation on the anode, the radicals contributed significantly to the CIP degradation achieved in the ECO system.

In conventional batch and flow-by configurations, \( \text{SO}_4^{2-} \) was not observed on the SnO\(_2\)-Sb anode (Santos et al., 2018). However, the unique confining effect of the permeable SnO\(_2\)-Sb anode appears to facilitate the formation of \( \text{SO}_4^{2-} \) within the RAF, as validated by the detection of a stable concentration of \( \text{S}_2\text{O}_8^{2-} \) (0.76 mg L\(^{-1}\)) in the RAF permeate (Fig. S7, Supporting Information). The pseudocapacitance of the RAF allows the electrosorption of \( \text{SO}_4^{2-} \), increasing the \( \text{SO}_4^{2-} \) concentration at the interface and facilitating the generation of \( \text{SO}_4^{2-} \) via reaction R(4) (Cai et al., 2019). In addition, the large amount of ‘OH produced in the interior of the RAF via reaction R(7) reacts with HSO\(_4^-\) to form \( \text{SO}_4^{2-} \) via reaction R(9). According to DFT calculations reported in the literature (Davis et al., 2014), the activation energy of reaction R (9) is sufficiently low for it to readily occur. Thereafter, ‘OH, together with \( \text{SO}_4^{2-} \), act as strong oxidants for the degradation of organic contaminants, while the superfluous radicals contribute to the formation of \( \text{S}_2\text{O}_6^{2-} \) in the solution (R10).

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{‘OH} + \text{H}^+ + e^- \quad \text{(R7)} \\
\text{SO}_4^{2-} + \text{H}^+ & \rightarrow \text{HSO}_4^- \quad \text{(R8)} \\
\text{HSO}_4^- + \text{‘OH} & \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \quad \text{(R9)}
\end{align*}
\]

\[
\begin{align*}
\text{SO}_4^{2-} & \rightarrow \text{SO}_4^{-} + e^- \\
\text{SO}_4^{-} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2^- \\
\text{SO}_4^{-} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2^- + \text{e}^- \\
\text{SO}_4^{-} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2^- + \text{e}^- \\
\text{SO}_4^{-} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2^- + \text{e}^- \\
\end{align*}
\]
SO$_4^{2-}$ + HSO$_3^{-}$ → S$_2$O$_7^{2-}$ + H$^+$ + e$^-$ \hspace{1cm} (R10)

This proposed mechanism was further validated by the results of comparative testing. A batch ECO test of the 3D porous SnO$_2$-Sb anode was conducted in a beaker containing 100 mL 0.1 M Na$_2$SO$_4$ solution. At applied cell potentials of 1.0–5.0 V, no S$_2$O$_7^{2-}$ was detected in the solution during the 2-h ECO treatment. In contrast, for the flow-through RAF in the ECO cell, the S$_2$O$_7^{2-}$ concentration in the permeate was as high as 0.78 mg L$^{-1}$ (Fig. S8, Supporting Information). Additionally, the RAF-based ECO treatment was conducted in an inert electrolyte (0.1 M NaClO$_4$) for comparison. In the inert NaClO$_4$ solution, the CIP removal was 11% lower than that in the Na$_2$SO$_4$ electrolyte (Fig. S9), implying the contribution of sulfate radicals during the flow-through ECO process. In addition, production of other oxidants could also possibly occur during the ECO process. The \(^\cdot\)OH radicals generated on the anode surface would react with each other to form H$_2$O$_2$ via reaction R11 and further produce hydroperoxyl radicals (HO$_2^\cdot$) via reaction R12 (Sires et al., 2014). The generation of O$_3$ could be also promoted by the reaction of \(^\cdot\)OH with O$_2$ (R13) (Canizares et al., 2009).

\[ 2\text{OH} → \text{H}_2\text{O}_2 \] \hspace{1cm} (R11)

\[ \text{OH} + \text{H}_2\text{O}_2 → \text{HO}_2^\cdot + \text{H}_2\text{O} \] \hspace{1cm} (R12)

\[ \text{O}_3 + 2\text{OH} → \text{O}_3 + \text{H}_2\text{O} \] \hspace{1cm} (R13)

Overall, it can be deduced that the ECO system using the novel RAF achieved ultrafast CIP degradation through direct oxidation and reactions with reactive radicals, namely \(^\cdot\)OH and SO$_4^{2-}$.

The degradation of CIP proceeded mainly through cleavage of the piperazine structure, hydroxylation of the quinolone ring, and defluorination (Yahya et al., 2014). The intermediate products of the CIP oxidation by the ECO treatment were determined by UPLC-QTOF-MS in this work. According to the MS data (Fig. S10), the possible intermediates were identified (Table S2). With the continuous strong oxidation by direct electron transfer and reactions with reactive radicals (\(^\cdot\)OH and SO$_4^{2-}$), the intermediates were degraded to small organic fragments and further to short aliphatic acids, which were finally oxidized by the RAF to CO$_2$ and H$_2$O.

3.5. Stability and feasibility of the RAF for ECO treatment

In addition to the electrocatalytic activity, the stability of the porous and freestanding RAF electrode was assessed. The stability test of the flow-through RAF was conducted in an ECO cell supplied continuously with CIP wastewater (10 \(\mu\)M CIP and 0.1 M Na$_2$SO$_4$) at a flux of 27 LMH. At an applied cell potential of 4.0 V, a CIP removal efficiency of nearly 100% was maintained for more than 200 h (Fig. 8a). Even after more than 200 h of this ECO treatment, the structure of the RAF was found to be stable, as characterized by XRD and SEM (Fig. 1, Fig. S11). These results demonstrate the high stability of the freestanding SnO$_2$-Sb anode for use as a permeable RAF in ECO applications, which overcomes the fundamental challenge of the low efficiency and short service life of the Ti-based SnO$_2$ anodes.

ECO treatment is also highly effective in mitigating the problem of antibiotics in wastewater discharge. In this regard, the antibiotic activity of the CIP wastewater was assessed using a diluted E. coli culture (see Text S5, Supporting Information for details). The addition of 6 mL of the CIP wastewater (10 \(\mu\)M CIP) in 30 mL of the growth mixture resulted in nearly 100% inhibition of E. coli growth (Fig. S12). In contrast, following a brief RAF-based ECO treatment, the addition of the treated permeate resulted in nearly zero inhibition of E. coli growth, an effect similar to that of adding DI water. These results highlight the efficiency of the RAF-based ECO treatment in eliminating antibiotics such as CIP from wastewater. In other words, rapid ECO process is effective in mitigating the problem of antibiotics in wastewater without generating byproducts that are toxic to microbial cells.

Considering that the low conductivity and the adversarial effect of some inorganic anions (such as HCO$_3^-$) in wastewater may hinder ECO efficiency, the practicality and effectiveness of the RAF-based ECO system in treating actual wastewater were evaluated. For this test, secondary effluent from a municipal wastewater plant (Stanley STW) in Hong Kong was collected and several target organic pollutants, namely CIP, MOX, MB, and RhB, were added individually (one pollutant for each test), without the addition of any other chemicals. As shown in Fig. 8b, the rapid ECO treatment removed at least 92% of each of the model contaminants, demonstrating the feasibility and versatility of the RAF in the ECO treatment of actual wastewater. Besides, the RAF-based ECO system has a much lower electric energy consumption rate (0.33 kWh m$^{-3}$) for treating antibiotics in wastewater (20 ppm CIP, at 4.0 V), compared with the ECO treatment using the state-of-the-art 2D SnO$_2$-Sb/Ti anode (11.81 kWh m$^{-3}$) (Wang et al., 2016), as well as the conventional biological wastewater treatment (0.80 kWh m$^{-3}$) (Singh et al., 2012). In summary, the RAF-based ECO technology can rapidly and completely remove antibiotics (e.g., CIP) and other emerging organic contaminants from actual wastewater for effective water pollution control.

4. Conclusions

A novel freestanding and permeable SnO$_2$-Sb anode was developed as a RAF that functions as both an anode and a filter in flow-through ECO process for wastewater treatment. The porous RAF without the Ti base substrate was fabricated by one-step compression and sintering method using (NH$_4$)$_2$CO$_3$ grains as the pore-forming agents. Forcing the antibiotics-containing wastewater through the micrometer-sized...
channels of the RAF improved the mass transport and vastly enlarged the electroactive surface area. Compared with the conventional flow-by configuration, the flow-through RAF exhibited a 12-fold increase in the mass transfer rate constant (60.7 × 10⁻⁷ m s⁻¹), a 5-fold increase in the CIP degradation rate constant (0.077 min⁻¹), and an 8-fold reduction in the energy consumption (0.31 kWh g⁻¹cat). In continuous single-pass operation with a cell potential of 4.0 V, more than 92% of the CIP was degraded at a filtration flux of 54 LMH and a retention time of only 1.7 min through the RAF. The reaction kinetics affirmed that the CIP was more effectively degraded in the interior flow through the RAF (contribution of 75%) than did in the bulk solution of the ECO cell. The robustness and stability of the RAF were demonstrated by its remarkable and stable CIP degradation efficacy of 99% during the long-term ECO test of 200 h. The mechanism of CIP degradation was elucidated using direct electron transfer and oxidation by ECO-generated radicals (OH and SO₄⁻). The SnO₂–SrFAB-based ECO cell performed well in treating actual municipal wastewater for effective degradation of antibiotics at a low energy consumption rate (0.33 kWh m⁻³). The development of RAFs will fundamentally advance the design and operation of the ECO process for toxic and recalcitrant organic pollutants in wastewater treatment.

CRediT authorship contribution statement

Chao Yang: Conceptualization, Investigation, Methodology, Writing—original draft. Yi Yang: Formal analysis, Visualization. Shanshan Shang: Formal analysis, Investigation. Pu Li: Methodology. Xiaoyan Li: Supervision, Methodology, Writing—review & editing, Funding acquisition.

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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Appendix A. Supplementary material

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References


