Hydroxyl multi-walled carbon nanotube-modified nanocrystalline PbO₂ anode for removal of pyridine from wastewater

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Abstract.

We prepared a hydroxyl multi-wall carbon nanotube-modified nanocrystalline PbO₂ anode (MWCNTs-OH-PbO₂) featuring high oxygen evolution potential, large effective area, and excellent electrocatalytic performance. The oxygen evolution potential and effective area of the MWCNTs-OH-PbO₂ electrode were 1.5 and 3.7-fold higher than the traditional PbO₂ electrode. Electrochemical degradation of pyridine in aqueous solution was investigated by using the MWCNTs-OH-PbO₂ anode. Based on pyridine decay rate (93.8%), total organic carbon reduction (84.6%), and energy consumption (78.8 Wh·L⁻¹·order⁻¹) under the optimal conditions, the MWCNTs-OH-PbO₂ electrode modified with MWCNTs-OH concentration of 1.0 g L⁻¹ exhibited higher electrochemical oxidation ability than the traditional PbO₂ electrode. The intermediate, hydroxypyridine, was found at the first stage of electrolysis. The primary mineralization product, NO₃⁻, was detected in aqueous solution after electrolysis. A possible electrochemical mineralization mechanism including two potential routes, i.e., *via* formation of small organic molecules by ring cleavage reaction and direct mineralization to CO₂ and NO₃⁻, was proposed. The results demonstrated that the MWCNTs-OH-PbO₂ electrode exhibited high efficiency for pyridine mineralization in aqueous solution under mild conditions.

Keywords: Electrochemical mineralization; Pyridine; PbO₂; Multi-walled carbon nanotube; Wastewater

1. Introduction

Pyridine is widely found in water, dust, and the atmosphere due to its broad industrial applications as a parent chemical, solvent, and processing additive [1,2]. The concentration of pyridine in industrial wastewater varies from 20 to 300 mg·L⁻¹ [3]. Previous research has indicated that pyridine wastewater is not amenable to biological treatment due to its complexity and toxicity [3,4]. Several strategies, including Fenton oxidation, sorption, catalytic wet oxidation, and photocatalysis [1,3,5,6], have been used to remove pyridine from wastewater. However, these processes are energy intensive and require strict operation conditions. Hence, the development of efficient and economical technologies for the elimination of pyridine from wastewater is critical.

Electrochemical oxidation is one kind of advanced oxidation processes to treat wastewater containing toxic or refractory organic pollutants. It has attracted much attention because it is automated, environmentally compatible, safe, and fast [7-9]. The anodic material directly affects the electrochemical oxidation efficiency of organic pollutants [10]. Some materials, such as graphite, RuO₂, and SnO₂, have been investigated to degrade pyridine; however, these materials required drastic conditions to cleave the pyridine ring and achieved low degradation efficiencies [11-13]. Thus, the development of new electrodes for the high efficient decomposition of pyridine is of great importance.

PbO₂ has been widely applied in electrochemical oxidation processes and exhibited high electro-catalytic activity under mild operation conditions [14]. Introducing active materials into the PbO₂ film can significantly improve the oxidation activity of PbO₂ electrodes [15-18]. Recently, multi-walled carbon nanotubes (MWCNTs) have been applied to different electrodes to obtain

larger surface areas for more contact between electrodes and reactants due to their high electrical conductivity, good chemical stability, and extreme mechanical strength [19-22]. For instance, carbon nanotubes (CNT)-metal nano-composites have high electrochemical activity and excellent stability [23,24]. The $\text{MnO}_2/\text{MWCNTs}$ composite has a relatively high specific capacitance and exhibits high stability [25]. The MWCNTs dopants can efficiently improve the electrocatalytic activity and the service life of the $\text{Ti}/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode [26-28]. However, the aggregation of MWCNTs in the polar liquid due to their hydrophobicity hampers MWCNTs doping into the PbO_2 layer [29,30]. Some studies have reported that the surfactant can hinder the aggregation of MWCNTs, but the addition of a surfactant into the electro-deposition solution can barely improve the hydrophilicity of the MWCNTs while still restricting the electrode practical applications, such as low oxygen evolution potential (OEP), low effective area, and complex preparation process [22,26,31,32].

To improve the hydrophilicity of MWCNTs, their surfaces are often tailored by covalent or non-covalent modification strategies [32-34]. Among the various types of surface modification strategies, deliberately grafting oxygen-containing functional groups at the open ends and sidewalls of MWCNTs is a popular and versatile approach [35,36]. However, to the best of our knowledge, there is still no report on the modification of a PbO_2 electrode by doping MWCNTs with oxygen-containing functional groups to degrade pyridine in aqueous solution.

The aim of this study was to prepare MWCNTs-OH-PbO_2 electrodes by adding hydroxyl modified MWCNTs in an electroposition solution to further improve the electro-catalytic activity of PbO_2 electrode. The physicochemical and electrochemical properties of the

MWCNTs-OH-modified PbO_2 electrode were characterized. The effects of MWCNTs-OH concentration, current density, plate distance and initial pyridine concentration on the electrochemical degradation kinetics of pyridine were investigated to evaluate the electro-catalytic activity of PbO_2 electrode. The removal of total organic carbon (TOC) and total nitrogen (TN) was determined to assess the mineralization of pyridine in aqueous solution. Furthermore, the degradation intermediates were analyzed and a possible mineralization pathway was then proposed. Finally, the energy consumption of pyridine degradation was evaluated.

2. Materials and Methods

2.1 Materials

The multi-walled carbon nanotubes (purity > 95%, outer diameter = 10 – 20 nm) were purchased from J&K Chemical Ltd. (Beijing, China). Sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), and potassium chloride (KCl) were obtained from Sinopharm (Beijing, China). Pyridine was supplied by Sigma-Aldrich (St. Louis, MO, USA). High Performance Liquid Chromatography (HPLC)-grade methanol for HPLC analyses was purchased from Sinopharm (Beijing, China). All chemicals used in the experiments were reagent grade or higher and were used as received without further purification.

2.2 Electrode Fabrication and Characterization

The C-OH group of MWCNTs-OH was prepared by a covalent surface modification strategy to improve the dispersion properties and enhance chemical interactions of MWCNTs [32]. The

middle layer of the Ti/SnO₂-Sb/PbO₂-MWCNT-OH electrode was prepared by a sol-gel method to achieve a uniform and well-adhered deposit [37]. The outer layer was deposited from 0.1 mol·L⁻¹ HNO₃ acidic medium containing 200 g·L⁻¹ Pb(NO₃), 0.5 g·L⁻¹ NaF, and 0-5 g·L⁻¹ MWCNTs-OH at a constant anode current density of 200 A·m⁻² for 2 h. The electrodeposition temperature was 65 ± 1 °C. Further details about the pretreatment and the preparation of PbO₂ electrode were provided in previous work [38]. The names of the six electrodes were abbreviated as bare PbO₂, 0.1-CNT-PbO₂, 0.5-CNT-PbO₂, 1.0-CNT-PbO₂, 2.0-CNT-PbO₂, and 5.0-CNT-PbO₂ for the electrodes modified by 0.0, 0.1, 0.5, 1.0, 2.0, and 5.0 g·L⁻¹ of MWCNTs-OH, respectively.

The linear sweep voltammetry (LSV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were conducted in a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). The LSV, CV, and EIS were all performed with a conventional three-electrode system. The MWCNTs-OH-PbO₂ electrodes (1 cm × 2 cm), platinum wire, and saturated calomel electrode (SCE) were used as working electrodes, an auxiliary electrode, and a reference electrode, respectively. Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) were carried out to determine the surface morphology and composition of the electrodes on a Hitachi S4800 instrument with an accelerating voltage of 15 kV. The phase composition analysis of the PbO₂ deposits (pristine electrode film) was performed by measuring the diffraction patterns using a Bruker HiStar general area detector diffraction system X-ray diffractometer (XRD) with Ni-filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) and a step size of 0.05°.

2.3 Electrochemical Experiments

The electrochemical cells were made of acrylic glass (length: 5 cm; width: 10 – 30 mm; height: 8 cm) (for details, see Figure S1 of the Supporting Information (SI)). The MWCNTs-OH-PbO₂ electrode (50 mm × 50 mm × 1 mm) and Ti electrode (50 mm × 50 mm × 1 mm) were used as the anode and cathode, respectively. The electrochemical experiments were carried out *via* batch processes. The influencing parameters including MWCNTs-OH concentration (0 – 5 g·L⁻¹), initial pyridine concentration (10 – 200 mg·L⁻¹), and current density (5 – 30 mA·cm⁻²) were investigated at a volume of 25 mL pyridine solution. The effect of the different plate distances (1 – 3 cm) on pyridine degradation was conducted with 25 – 75 mL pyridine solution. Ten mmol·L⁻¹ NaClO₄ was used as the supporting electrolyte, and a magnetic stirrer (IKA-RCT, Germany) was equipped to increase the mass transfer at a stirring rate of 800 r·min⁻¹.

2.4 Instrumental Analysis

The concentrations of the pyridine were determined via HPLC-UV (Dionex U3000, USA). The separation was performed with an Agilent HC-C18 column (4.6 mm × 150 mm, 5 μm) at 30°C. The mixture of methanol and water (50:50, V:V) was used as the mobile phase at a flow rate of 1 mL min⁻¹. The sample injection volume was 25 μL, and the UV detector was set at 210 nm. The identification of intermediates used an Accurate-Mass-LC/MA 6250 (Agilent, USA) equipped with an electrospray ionization (ESI) source operating in the positive ion mode (Text S1).

The concentration of nitrogen inorganic ions (NO₂⁻, NO₃⁻) was measured by ionic chromatography (ICS-1000, Dionex, USA). The TOC and TN in aqueous solutions were analyzed with an Analyzer multi N/C UV (Analytic Jena, Germany) according to the 800°C combustion

catalytic oxidation method.

3. Results and Discussion

3.1 Electrode Characterization

Table 1 summarizes the physicochemical properties of PbO_2 electrodes including its physical appearance, crystal structure, crystallite size, and electrochemical performances. The microstructure of the PbO_2 deposits was characterized by SEM-EDX to assess the influence of the MWCNTs-OH concentration on the surface morphologies of the PbO_2 electrodes. The surface of the electrode without modification (bare PbO_2) exhibited a typical pyramidal shape. Uniform deposits of 1.0-CNT- PbO_2 were obtained to yield perfect surface coverage with crystallites of typical pyramidal shape (Figure 1). The formation of typical-structured PbO_2 electrodeposits has also been reported in other works [39,40]. Others had different shapes and bigger size of PbO_2 particles (detailed description of other electrodes is shown in Figure S2 of the SI). The results showed that the morphologies of the coatings exhibited different physical appearances. The introduction of MWCNTs-OH into PbO_2 deposits could significantly affect the surface morphology. This difference of the physical appearance was ascribed to the blockage of charge transfer from PbO_2 to MWCNTs-OH because MWCNT has a higher work function than PbO_2 , and there is the Schottky barrier between PbO_2 and MWCNTs-OH [41,42]. As a consequence, MWCNTs-OH acted as electron barrier to hinder the successive growth of the big pyramidal PbO_2 particles. Then the PbO_2 crystallites grew on the surface of pyramidal PbO_2 particles (Scheme 1).

Scheme 1 here

Table 1 here

Figure 1 here

The phase composition of bare PbO_2 and 1.0-CNT- PbO_2 electrodes were determined by XRD (Figure 1a). The strong peaks at 49.1° and 62.4° could be attributed to the diffraction from the (211) and (301) planes of PbO_2 , respectively, showing a relative 100% intensity on 1.0-CNT- PbO_2 . Other diffractograms, including MWCNTs-OH for comparison, are shown in Figure S3. The mean crystallite size (L_{hkl}) was estimated roughly from the halfwidth of the peaks at 25.5° , 31.8° , 36.1° , 49.1° and 62.4° (Table S1) according to the Debye-Scherrer equation [43]. The crystal size of electrodes decreased from 9.4 nm to 5.6 nm with the increasing concentrations of MWCNTs-OH (Table 1). The EDS analysis in Figure S4 indicated that the MWCNTs-OH was doped into the PbO_2 film. It is well known that multifunctional dopants can occupy the active sites of the deposit surface and inhibit the crystal growth [44]. The inhibitor (i.e. WMCNTs-OH) could only occupy a minority of the active sites at low concentrations of MWNCTs-OH. Continued growth of the PbO_2 deposit was not affected by MWCNTs-OH in the most of active zones, resulting in large crystal sizes. A large amount of MWCNTs-OH occupied statistically the active sites of PbO_2 crystals. The diffusion of the lead ions to the active sites was hindered by MWCNTs-OH, and the growth of PbO_2 crystals was disturbed. Lead ions would nucleate on those sites occupied by MWCNTs-OH. The size of PbO_2 crystals was then decreased. A similar phenomenon was also found in other studies [30,44,45],

but the size of the PbO₂ crystallite in this study was smaller. Hence the increasing concentration of MWCNTs-OH decreased the crystal size of PbO₂ electrode by disturbing the continuous crystal growth of PbO₂. Some researchers mentioned that more crystal particles on electrode surface could result in higher electrocatalysis activity of PbO₂ electrode [30]. Thus, PbO₂ electrodes modified with different concentrations of MWCNTs-OH were structurally and morphologically compared to identify the differences of electrocatalytic efficiencies.

A high OEP is desirable in the development of electrode material for wastewater treatment. The OEP of the electrodes was determined via linear sweep voltammetry (Figure S5 of the SI). Figure 1b shows the linear voltammograms of bare PbO₂ and 1.0-CNT-PbO₂ electrodes in 0.5 M Na₂SO₄ at 25°C with a scan rate of 50 mV·s⁻¹. According to the polarization curves, the PbO₂ electrode without modification had an OEP value of 1.65 V (*vs.* SCE) — this was similar to other studies [18,47]. The OEP values for 0.5-CNT-PbO₂, 1.0-CNT-PbO₂, and 2.0-CNT-PbO₂ electrodes were approximately 1.96 V, 2.48 V, and 1.98 V (*vs.* SCE), respectively, which were higher than those in previous studies [38,48]. The OEP value of 1.0-CNT-PbO₂ anode was close to that of the BDD anode (2.75 *vs.* SCE) [49]. We concluded that the OEP decreased in the following order: 1.0-CNT-PbO₂ (> 2.0-CNT-PbO₂) > 0.5-CNT-PbO₂ > 0.1-CNT-PbO₂ > bare PbO₂ (> 5.0-CNT-PbO₂). This difference of OEP was mainly attributed to the following reasons: (1) the addition of MWCNTs-OH in the electrode could hinder the movement and expansion of the free oxygen atoms to the electrode interior, which decreased the transfer coefficient of oxygen evolution reaction to 0.29 with a Tafel slope of 207.1 mV dec⁻¹ on the surface of the electrode (see Table S2) and increased the OEP of electrodes; (2) MWCNTs-OH in the electrode decreased the internal stress

between PbO₂ crystals and then led to few cracks on the electrode surface. This surficial structure of the electrode could inhibit water diffusing to the interior of the electrode film, resulting in the decrease of oxygen evolution reaction and the increase of OEP. (3) the excessive addition of MWCNTs-OH (2.0, 5.0 g L⁻¹) destroyed the PbO₂ crystal structure and exposed the Ti layer which had a low value of OEP (Figure S2), leading to the decrease of OEP.

The effective area of the electrode was estimated from the cyclic voltammograms (Figure S6).

The effective areas of these electrodes were estimated according to Eq. (1)

$$I_p = 2.69 \times 10^5 n^{3/2} D_0^{1/2} v^{1/2} A C_0 \quad (1)$$

where I_p is the peak current (A), n is the stoichiometric number of electrons involved in electrode reaction (for single charge-transfer process, $n = 1$), D_0 is the diffusion coefficient for [Fe(CN)₆]³⁻ (7.6×10^{-6} cm²/s), v is the scan rate (mV·s⁻¹), A is the effective area (cm²), and C_0 is the bulk concentration (0.01 M). Table 1 shows that the effective areas of the electrodes increased from 30.3 cm² to 110.6 cm² as the concentration of MWCNTs-OH increased from 0 to 1.0 g·L⁻¹ and then decreased to 73.8 cm² as the MWCNTs-OH concentration increased to 5.0 g·L⁻¹. The largest effective area was obtained from the 1.0-CNT-PbO₂ electrode. The effective areas of all electrodes were much higher than the geometric surface area of the electrodes (2 cm²). The SEM and XRD results suggested that the addition of MWCNTs-OH accelerated the growth of PbO₂ crystallites on the PbO₂ particles and improved the porosity of the PbO₂ electrodes, which resulted in large effective area. The large effective area improved the possibility of the pollutant diffusing from solution to electrode surface, which would be beneficial for the electrocatalytic performance of the

electrode.

The EIS was used to elucidate the effect of MWCNTs-OH on the interfacial properties of the PbO_2 electrode. The Nyquist plot could be interpreted in terms of the equivalent circuit (Figure S7). The EIS results of bare PbO_2 and 1.0-CNT- PbO_2 electrodes are shown in Figure 1c. The resistance values of electrode/solution are shown in Table 1. The results indicated that bare PbO_2 electrode exhibited the smallest semicircle radius of these electrodes, suggesting that doping MWCNTs-OH increased the charge-transfer resistance of the interface of electrode/solution. The charge-transfer resistance increased with the increasing concentration of MWCNTs-OH, which resulted in the increase of the applied voltages during the batch experiment (as shown in Table 2). This was probably because the separation of gas molecule from the porous surface of electrode during the electrochemical process blocked the generated electrons to transfer through the interface of electrode/solution, and then lead to the increase of the charge-transfer resistance. It should be noted that the applied voltage of 1.0-CNT- PbO_2 was as same as that of bare PbO_2 . This might be ascribed to the application of a magnetic stir which eliminated the influence of the separation of gas molecule from the porous surface, and enhanced the diffusion of supporting electrolyte to the porous surface to increase the charge transfer. Hence the addition of MWNCTs-OH greatly affected the interfacial charge-transfer resistance of the PbO_2 electrode but slight influence appeared on the application of the electrodes under the operational conditions. In addition, the accelerated life tests of bare PbO_2 and 1.0-CNT- PbO_2 showed that the service life of 1.0-CNT- PbO_2 was improved to 504 h, which was 1.5 times longer than that of bare PbO_2 (Figure S8). In this study, MWCNTs-OH were embedded in the PbO_2 matrix to reinforce the PbO_2 film. The co-deposition of MWCNTs-OH

acted as barriers to baffle the penetration of the electrolyte, and eliminate the generation of high pressure between PbO₂ particles. Therefore the MWCNTs-OH enhanced the chemical stability of PbO₂ electrode.

3.2 Electrochemical Degradation Kinetics of Pyridine

The effects of MWCNTs-OH concentration (0 – 5 g·L⁻¹), initial pyridine concentration (10 – 200 mg·L⁻¹), electrode distance (10 – 30 mm), and applied current density (5 – 30 mA·cm⁻²) on the degradation kinetics of pyridine are shown in Figure 2. In all experiments, the degradation followed pseudo-first-order kinetics. The rate constants (*k*) values were calculated from linear regression of the corresponding semi-log plots. The degradation rate, mineralization rate, *k*, half-lives (*t*_{1/2}), *R*², and correlation coefficients are summarized in Table 2. These results showed that pyridine could be effectively degraded during the electrochemical process.

Table 2 here

The influence of PbO₂ electrodes modified with different concentrations of MWCNTs-OH on the electrochemical degradation performance of pyridine was investigated. Figure 2a shows that the degradation rates of pyridine on MWCNTs-OH-PbO₂ electrodes increased as a function of MWCNTs-OH (and increased to 1.0 g·L⁻¹), but then decreased when the amount of MWCNTs-OH reached 5.0 g·L⁻¹. The maximal pyridine removal rate of 75.4% was observed with 1.0-CNT-PbO₂ electrodes. The results indicated that the introduction of MWCNTs-OH could enhance the electrochemical degradation performance of pyridine. However, high concentrations of

MWCNTs-OH ($> 1.0 \text{ g}\cdot\text{L}^{-1}$) in the electrodeposition solution might weaken the performance of the PbO_2 electrode. The efficiencies of the six electrodes in terms of pyridine degradation were: $1.0\text{-CNT-PbO}_2 > 2.0\text{-CNT-PbO}_2 \approx 0.5\text{-CNT-PbO}_2 > 0.1\text{-CNT-PbO}_2 > \text{bare PbO}_2 > 5.0\text{-CNT-PbO}_2$. This was similar to the results of OEP and the effective areas. The highest OEP with the 1.0-CNT-PbO_2 electrode led to a low side reaction of oxygen formation and a high current efficiency during electrochemical process. The largest effective area of 1.0-CNT-PbO_2 electrode increased the possibility that the pyridine molecules contacted with the active sites on the electrode. This resulted in high pyridine degradation. Moreover, the TOC removal rates after 90 min of electrolysis were 24.9%, 32.5%, 36.0%, 52.0%, 35.0%, and 22.0% for bare PbO_2 , 0.1-CNT-PbO_2 , 0.5-CNT-PbO_2 , 1.0-CNT-PbO_2 , 2.0-CNT-PbO_2 , and 5.0-CNT-PbO_2 anodes, respectively. Thus, 1.0-CNT-PbO_2 electrode was adopted for subsequent experiments for its better performance on the mineralization of pyridine than other electrodes.

Figure 2 here

Figure 2b shows the effect of the applied current density on the degradation of $100 \text{ mg}\cdot\text{L}^{-1}$ pyridine. The degradation rate of pyridine increased significantly from 65.1% to 99.9% as a function of the increasing applied current density. As shown in Table 1, the half-life ($t_{1/2}$) values were 57.8 and 53.3 min at 5 and $10 \text{ mA}\cdot\text{cm}^{-2}$, respectively, implying that low current densities ($\leq 10 \text{ mA}\cdot\text{cm}^{-2}$) could not significantly accelerate the decay rate of pyridine. In contrast, the $t_{1/2}$ value of pyridine at $10 \text{ mA}\cdot\text{cm}^{-2}$ was 2.1 - and 3.9 - fold longer than those at 20 and $30 \text{ mA}\cdot\text{cm}^{-2}$,

respectively. This indicated that high current densities ($\geq 20 \text{ mA}\cdot\text{cm}^{-2}$) could significantly accelerate the pyridine degradation rate. This was likely because the current density controlled the electron transfer and $\bullet\text{OH}$ generation on the electrode surface. In turn, this governed the degradation efficiency of pyridine on the anode (Figure S9 proved that pyridine did not transfer electron directly to anode). Moreover, the TOC removal rates after 90 min of electrolysis increased from 31.0% to 90.6% when the current density increased from 5 to $30 \text{ mA}\cdot\text{cm}^{-2}$. The results confirmed that pyridine and its byproducts could be mineralized in a short electrolysis time. Subsequently, a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ was chosen to investigate the effects of other factors on pyridine degradation.

The effect of plate distance on pyridine degradation efficiency was determined at distances ranging from 1 to 3 cm. Figure 2c shows that the pyridine oxidation rate decreases significantly with the increasing distance between the anode and cathode. A rapid destruction of pyridine was observed at an electrode distance of 1 cm with over 90% disappearance after 90 min. At a plate distance of 2 and 3 cm, the degradation efficiencies were 75.4% and 68.5%, respectively. The k value at a plate distance of 1 cm was 0.028 min^{-1} (Table 2), which is approximately 1.7 - and 2.0 - fold higher than those with plate distances of 2 and 3 cm, respectively. The degradation efficiency considerably decreased with the increasing plate distance. The TOC removal rate at 1 cm was higher than those at 2 and 3 cm, indicating that a shorter plate distance improved the mineralization rates of pyridine. The current distribution was the most significant parameter affecting the performance of the electrochemical system. The increasing plate distance worsened the current density distribution due to the decrease of the conductivity of liquid between the anode and cathode

[15,50]. Thus, a long plate distance was not beneficial for electrochemical degradation of pyridine in aqueous solution. More electrolysis time was required due to the long diffusion distance.

The pyridine degradation efficiency at initial concentrations of 10 – 200 mg·L⁻¹ is over 85% after 60 min (Figure 2d). The *k* values for the initial pyridine concentrations of 50 – 150 mg·L⁻¹ were similar to each other, suggesting that the electrochemical reaction was diffusion-controlled, which is a typical phenomenon for degradation with low concentration reactants [14]. The *k* value was 0.192 min⁻¹ at the initial concentration of 10 mg·L⁻¹, which is much higher than that at the initial concentrations of 50 – 200 mg·L⁻¹. The hydroxyl radical generated in the electrochemical system at a given current density is identical [48,51]. As a consequence, pyridine molecules were more likely to be attacked by hydroxyl radicals at a lower pyridine concentration solution due to the higher rate of transfer of the hydroxyl radical to the pyridine — this resulted in a higher *k* value. The *k* values decreased with the increasing pyridine concentrations (150 mg·L⁻¹ to 200 mg·L⁻¹), suggesting that only a portion of the pyridine molecules could be attacked by hydroxyl radicals at the beginning of the electrolysis. As shown in Table 2, the TOC removal rate decreases with the increasing concentrations of pyridine. The TOC removal rates were 97.2% and 93.2% at 10 and 50 mg·L⁻¹ of pyridine solution, respectively. These results indicated that the 1.0-CNT-PbO₂ anode had an excellent performance for pyridine degradation. Previous studies have investigated the degradation of pyridine by microwave radiation, biodegradation, and photocatalysis [52-54]. The degradation efficiencies of pyridine were presented in Table S3 of the SI. It could be concluded from the results that the degradation efficiencies of pyridine in this study were higher than those by above technologies, indicating that the electrochemical oxidative process is an efficient technology

for the elimination of pyridine from wastewater.

3.3 Mechanism of Electrochemical Mineralization of Pyridine

The mineralization of a heterocyclic compound is accompanied by the formation of carbon dioxide and inorganic ions. The release of inorganic ions is an indicator of pyridine mineralization. Upon bond cleavage of the pyridine molecules, the N atom would transform to NO_3^- and/or NO_2^- . IC determined the concentrations of these ions during the mineralization of $100 \text{ mg}\cdot\text{L}^{-1}$ of pyridine at $20 \text{ mA}\cdot\text{cm}^{-2}$. Figure 3 shows the changes in NO_3^- -N, and TN concentrations as well as the corresponding pyridine and TOC removal rates. No measurable amount of NO_2^- was detected during the electrochemical degradation of pyridine. The NO_3^- -N accumulated to $4.9 \text{ mg}\cdot\text{L}^{-1}$ after 30 min of electrolysis. Subsequently, the NO_3^- -N concentration decreased to $1.1 \text{ mg}\cdot\text{L}^{-1}$ after 90 min of electrolysis. The TN concentration decreased gradually from $17.7 \text{ mg}\cdot\text{L}^{-1}$ to $10.42 \text{ mg}\cdot\text{L}^{-1}$ as a function of electrolysis time. In previous studies, the NO_3^- -N could be reduced electrochemically [15,56,57]. The NO_2^- -N determined in our study was below the detection limit, which implied that the NO_3^- -N was reduced to gas (such as nitrogen) at the cathode. The loss of NO_3^- -N decreased the amount of TN in the electrochemical process. NO_3^- was found in the study, indicating that the pyridine ring was cleaved by the hydroxyl radical.

Figure 3 here

According to the Gibbs free energy of the transition states, the reaction between a pyridine and the hydroxyl radical occurs easily on the meta position of the pyridine [12,58,59]. One intermediate

(m/z 96.9) with the same mass as hydroxypyridine was detected in the solution (Figure S10). The dihydroxypyridine was determined during the electrochemical degradation of pyridine [12]. Dihydroxypyridines including 2,3-dihydroxypyridine and 3,5-dihydroxypyridine were also identified during the biodegradation of pyridine [60,61].

Figure 4 here

On the basis of the detected intermediates, a major electrochemical oxidation pathway was proposed, as shown in Figure 4, including the detected products and hypothetical intermediates in the dashed box. The 1.0-CNT-PbO₂ electrode was a typical non-active electrode, and it produced a large amount of hydroxyl radicals [48,58]. These hydroxyl radicals attacked the meta- position of pyridine and formed 3-hydroxypyridine. Subsequently, the 3-hydroxypyridine could be further attacked by the hydroxyl radical at the ortho- position or another meta- position to form 2,3-dihydroxypyridine or 3,5-dihydroxypyridine. After dehydrogenation, the pyridine ring undergoes cleavage with the formation of malonic, maleic, formic acids, and NO₃⁻. Through successive hydroxylation of these primary byproducts, the pyridine could be mineralized to CO₂, H₂O, and NO₃⁻. The NO₃⁻ was further reduced to N₂ at the cathode.

3.4 Energy Consumption

The energy consumption estimation is important to evaluate the application prospects of a technology. Thus, the economic feasibility of pyridine degradation with all operational parameters

was evaluated by determining the energy costs. The time needed to degrade pyridine was calculated by the k values shown in Table 2. The following equation was used to determine the time:

$$t = -1 / k \ln (C_t / C_0). \quad (3)$$

where t is the time (h) needed to degrade pyridine, k is the first order rate constant (min^{-1}), C_0 is the initial concentration of pyridine ($\text{mg}\cdot\text{L}^{-1}$), and C_t is the effluent concentration ($\text{mg}\cdot\text{L}^{-1}$). The energy consumption ($\text{Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$) can be determined using the following equation:

$$\text{EE/O} = I \times U \times t / (V \times \ln(C_0 / C_t)), \quad (4)$$

where EE/O is the electrical efficiency per log order reduction ($\text{Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$), I is the applied current (A), and U is the applied average voltage (V).

As the dopant concentration of MWCNTs-OH increased from 0 to $1.0 \text{ g}\cdot\text{L}^{-1}$, the EE/O decreased from 106.9 to $49.9 \text{ Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$, and then EE/O increased to $127.9 \text{ Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$ when the dopant concentration increased to $5.0 \text{ g}\cdot\text{L}^{-1}$. The energy cost at a dopant concentration of $1.0 \text{ g}\cdot\text{L}^{-1}$ MWCNTs-OH was 2.1 and 2.6 times lower than those at 0 and $5.0 \text{ g}\cdot\text{L}^{-1}$ of MWCNTs-OH, respectively, indicating that the PbO_2 electrode modified by $1.0 \text{ g}\cdot\text{L}^{-1}$ of MWCNTs-OH had a lower energy consumption than the other electrodes. As the applied current density increased from 5 to $30 \text{ mA}\cdot\text{cm}^{-2}$, the EE/O of the pyridine degradation increased from 29.1 to $124.7 \text{ Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$. The energy cost at $5 \text{ mA}\cdot\text{cm}^{-2}$ was 4.3 times lower than that at $30 \text{ mA}\cdot\text{cm}^{-2}$, indicating that a higher applied current density led to a higher energy cost. However, the lower applied current density required a longer residence time. The applied current density between 10 and $20 \text{ mA}\cdot\text{cm}^{-2}$ was a reasonable choice due to the relatively low energy cost ($57.6 - 78.8 \text{ Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$) and the relatively short residence time. The energy cost was $20.7 \text{ Wh}\cdot\text{L}^{-1}\cdot\text{order}^{-1}$

at a plate distance of 1 cm. This was much lower than the values of 40.4 and 39.5 Wh·L⁻¹·order⁻¹ at 2 cm and 3 cm of plate distance, respectively. With the increasing electrode distance, the electrolysis cell resistance increased, and the electrode diffusion distance became longer. This led to the increasing energy costs. The EE/O at different initial concentrations followed the order of EE/O₂₀₀ ≈ 1.4 EE/O₁₅₀ ≈ 1.4 EE/O₁₀₀ ≈ 1.4 EE/O₅₀ ≈ 9.4EE/O₁₀. Since 1.0-CNT-PbO₂ had higher oxidation rate, it consumed less energy than other electrodes. Under optimal conditions, the energy cost on 1.0-CNT-PbO₂ anode was 0.48 – fold of that on the bare PbO₂ anode (Table S4). The results suggested that the electrocatalytic method could be a feasible alternative for the treatment of wastewater containing pyridine.

4. Conclusion

A hydroxyl multi-wall carbon nanotube-modified nanocrystalline PbO₂ anode with 2.48 V (vs. SCE) of oxygen evolution potential and 110 cm² of effective area was prepared. According to the degradation efficiency, mineralization rate, and energy consumption, the optimal operating parameters for the electrochemical treatment of pyridine were 20 mA·cm⁻² and 1 cm with 1.0-CNT-PbO₂ anode. Under optimal conditions, the degradation rate and mineralization rate of pyridine on 1.0-CNT-PbO₂ anode were 1.3 - and 1.6 - fold, respectively, of those on bare PbO₂ anode; the energy consumption on 1.0-CNT-PbO₂ anode was 0.48 – fold of that on the bare PbO₂ anode. The results demonstrated that the MWCNTs-OH could hinder the continued growth of PbO₂ crystals to obtain a high OEP and a large effective area on the PbO₂ electrode. The 1.0-CNT-PbO₂ electrode with higher OEP and larger effective area exhibited high efficiency for mineralizing

pyridine under mild conditions, which was a promising anode for the treatment of contaminated water.

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Table 1. The physicochemical and electrochemical properties of six PbO₂ electrodes modified with different amounts of MWCNTs-OH. ^{*}

MWCNTs-OH (g·L ⁻¹)	Physicochemical and electrochemical properties of the PbO ₂ deposit								
	Physical appearance			Surface analysis			Electrochemical performance		
	Color ^a	Optical reflectivity	Quality	Phase ^b	Size ^c (nm)	Shape ^d	E _l ^e (V)	R _c ^f (Ω)	A ^g (cm ²)
0	grey	Shiny	Uniform	β	9.4	Pyramidal	1.65	115.3	30.3
0.1	grey	Matte	Uniform	β	7.1	Pyramidal and rounded	1.69	2106	46.7
0.5	grey/black	Matte	Uniform	β	7.2	different degree of porosity	1.96	2669	61.8
1.0	black	Matte	Uniform	β	6.8	Pyramidal	2.48	2369	110.6
2.0	black	Matte	Pitted	β	5.7	different degree of porosity	1.98	4801	64.8
5.0	black	Matte	Cracked	β	5.6	different degree of porosity	1.32	5536	73.8

^{*}The physical appearance was assessed visually, whereas surface analysis carried out by XRD and SEM-EDX allowed determination of the phase distribution, crystallite size, and shape. The electrochemical performance was tested by LSV, CV and EIS to determine the oxygen evolution potential, slope of peak current versus square root of scan rate and resistance.

^a Color of the PbO₂ deposit.

^b Crystal structure by XRD.

^c Crystallite size by XRD.

^d Morphology by SEM.

^e Oxygen evolution potential (vs. SCE)

^f Interfacial resistance of electrodes/solution

^g Effective area

Table 2. The degradation ratios, mineralization ratios, rate constant (k), half-lives ($t_{1/2}$), correlation coefficient (R^2), average voltage (U), and EE/O of electrochemical degradation of pyridine over CNT-PbO₂ electrode at different experimental parameters.*

Parameters		Degradation ratios (%)	Mineralization ratios (%)	k	$t_{1/2}$ (min)	R^2	U (V)	EE/O Wh·L ⁻¹ ·order ⁻¹
CNT concentration, g·L ⁻¹ ($C_0 = 100 \text{ mg L}^{-1}$)	0	49.0	24.9	0.007	99.0	0.990	7.8	106.9
	0.1	50.5	32.5	0.008	86.6	0.986	7.7	92.3
	0.5	60.6	36.0	0.010	69.3	0.980	7.5	72.0
	1	75.4	52.0	0.015	46.2	0.997	7.8	49.9
	2	56.8	35.0	0.009	77.0	0.987	8.0	85.2
	5	43.4	22.0	0.006	115.5	0.981	8.0	127.9
Current density, mA·cm ⁻² ($C_0 = 100 \text{ mg·L}^{-1}$)	5	65.1	31.0	0.012	57.8	0.982	7.3	29.1
	10	75.4	52.0	0.013	53.3	0.995	7.8	57.6
	20	93.8	84.6	0.028	24.6	0.970	11.5	78.8
	30	99.0	90.6	0.051	13.6	0.998	22.1	124.7
Plate distance, cm ($C_0 = 100 \text{ mg·L}^{-1}$)	1	93.8	84.6	0.028	24.6	0.970	7.8	20.7
	2	75.4	43.6	0.016	43.3	0.996	13.5	40.4
	3	68.5	38.8	0.014	49.5	0.986	17.3	39.5
Initial concentration ($C_0, \text{ mg·L}^{-1}$)	10	99.7	97.2	0.192	3.6	0.987	7.5	3.7
	50	91.4	93.2	0.028	24.8	0.991	7.6	26.0
	100	93.8	84.6	0.028	24.6	0.970	7.8	26.7
	150	93.7	65.2	0.032	21.7	0.986	8.4	25.9
	200	86.7	57.9	0.024	28.9	0.956	8.8	35.2

*Supporting electrolyte of $10 \text{ mmol L}^{-1} \text{Na}_2\text{SO}_4$, reaction time of 90 min, and n of 7.

Figure captions:

Scheme 1. Formation process of MWCNTs-OH-PbO₂ eletrode.

Figure. 1. SEM image of bare PbO₂ electrode modified with 1.0 g·L⁻¹ MWCNT-OH (1.0-CNT-PbO₂ electrode). Inset: (a) XRD spectra; (b) LSV; and (c) EIS.

Figure. 2. Effect of different factors on the degradation ratio or kinetics of 100 mg·L⁻¹ pyridine in 10 mmol·L⁻¹ Na₂SO₄ at 25°C. (a) Effect of MWCNTs-OH concentration at plate distance of 1 cm at current density of 10 mA·cm⁻². (b) Effect of current density at plate distance of 1 cm. (c) Effect of plate distance at current density of 20 mA·cm⁻². (d) Effect of initial concentration at plate distance of 1 cm and current density of 20 mA·cm⁻².

Figure. 3. The NO₃⁻-N and TN concentrations change and correlate to pyridine and TOC removal rates as a function of electrolysis time. (Current density of 20 mA·cm⁻², plate distance of 1 cm, pyridine of 100 mg·L⁻¹, and 1.0-CNT-PbO₂ electrode).

Figure 4. Proposed pathway for electrochemical degradation of pyridine by anodic oxidation on a 1.0-CNT-PbO₂ electrode.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Graphical Abstract