

Article

Upcycling Textile White Mud to Fabricate MIL-125-Derived Amorphous $\text{TiO}_2\text{@C}$: Effective Electrocatalyst for Cathodic Reduction of Antibiotics

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Abstract: Cathodic reduction is a green and promising remediation strategy for reducing the antibacterial activity of antibiotic contaminants and increasing their biodegradability. However, the lack of cost-effective electrocatalysts has restricted its application. In this study, we upcycled textile white mud by separating 1,4-dicarboxybenzene (BDC) and fabricating MIL-125(Ti)-derived amorphous $\text{TiO}_2\text{@C}$ ($\text{TiO}_2\text{@C-W}$) as a functional electrocatalyst. The separated BDC from white mud shows lower crystallinity than BDC chemicals, but the resulting $\text{TiO}_2\text{@C-W}$ features a much higher degree of oxygen vacancies and a 25-fold higher specific surface area than that of $\text{TiO}_2\text{@C}$ derived from BDC chemicals. With florfenicol (FLO) as a probe, $\text{TiO}_2\text{@C-W}$ exhibits similar cathodic reductive activity (0.017 min^{-1}) as commercial $\text{Pd}(3 \text{ wt.}\%)/\text{C}$ (0.018 min^{-1}) does, which was 1.4 and 3.7 times higher than that of oxygen vacancy-engineered TiO_2 and $\text{TiO}_2\text{@C}$, respectively. The as-fabricated $\text{TiO}_2\text{@C-W}$ could not easily remove FLO via the oxygen reduction reaction-based pathway with the applied bias for cathodic reduction. Though the activity of $\text{TiO}_2\text{@C-W}$ undergoes a slight decline with continuous running, more than 80% of 20 mg L^{-1} FLO can still be reduced in the eighth run. Water chemistry studies suggest that a lower initial solution pH boosts the cathodic reduction process, while common co-existing anions such as Cl^- , NO_3^- , HCO_3^- , and SO_3^{2-} show a limited negative impact. Finally, $\text{TiO}_2\text{@C-W}$ shows reductive activity against several representative antibiotics, including nitrofurazone, metronidazole, and levofloxacin, clarifying its potential scope of application for antibiotics (e.g., molecules with structures like furan rings, nitro groups, and halogens). This study couples the upcycling of textile white mud with the remediation of antibiotics by developing functional electrocatalysts, and offers new insights for converting wastes from the printing and dyeing industry into value-added products.

Keywords: textile white mud; 1,4-dicarboxybenzene; electrocatalyst; cathodic reduction; antibiotics



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1. Introduction

The increasing use of antibiotics has brought global health concerns. As reported, more than 50,000 cases of antibiotic-resistant infections occur annually in Europe and the United States [1]. Due to a relatively lower removal efficiency, antibiotics have been continually released into the natural environment (e.g., soil and aquatic ecosystems), and this could result in the evolution of novel antibiotic-resistant genes and bacteria. Therefore, antibiotics have been widely accepted as contaminants of emerging concern (CECs) [2,3]. Florfenicol (FLO) is a fluorinated chloramphenicol antibiotic that has a broad spectrum of antibacterial activity that includes all organisms sensitive to chloramphenicol, Gram-negative

bacilli, Gram-positive cocci, and other atypical bacteria such as mycoplasma. It has been used as an antimicrobial agent for the treatment of bovine respiratory disease and foot rot in aquaculture [4,5], and it has been detected in tap water with a median concentration of 8.9 ng L^{-1} [6]. Water has been recognized as a receptor for mass fluxes of antibiotics with the emission of waste streams [7]. The development of elimination technology for antibiotics in aqueous settings is highly desired. Various treatment strategies for removing aqueous antibiotic contaminants have been proposed [8]. The biological processes, filtration, and coagulation/flocculation/sedimentation are the most used in conventional wastewater treatment plants. However, the application of biological processes is limited by the poor selectivity [8]. Microbial reductive degradation of antibiotics has been reported to be an economic and environmentally-friendly strategy. Nevertheless, complete elimination was shown to be a time-consuming process [9]. Catalytic degradation by nanomaterials is another option with high reaction rates [10–12]; however, the drawbacks of nanomaterials, such as aggregation, passivation, and potential environmental risks, are still in suspense [13,14]. Given that traditional biodegradation methods cannot effectively remove antibiotics, it is necessary to reduce antibacterial activity with a feasible pretreatment approach before waste streams enter the biological treatment unit [15,16].

Cathodic reductive remediation refers to the degradation (conversion) process of refractory contaminants triggered by continuous electrons from the cathode, which is effective for numerous pollutants including halogenated aliphatic/aromatic compounds, nitroaromatics, and antibiotics with specific structures [17–20]. For antibiotic contaminants, this remediation technology can simultaneously achieve the detoxification and reduction of antimicrobial activity via reaction steps such as dehalogenation, nitro group reduction, and ring-opening [18,21]. Electrocatalysts play an essential role in cathodic reductive remediation, and both noble metals and non-noble metal oxides (or sulfides, phosphides, etc.) have shown their catalytic potentials for this application up to now [22–25]. Recently, we reported that titanium oxide as a semiconducting material could be engineered with vacancies to effectively catalyze the cathodic reductive degradation of florfenicol (a typical wide-spectrum antibiotic agent) [26]. This strategy overcomes the intrinsic poor conductivity and rare active sites of transition metal oxides, and is expected to convert these inert materials into high-performance electrocatalysts.

Metal–organic frameworks (MOFs) are a class of crystalline micro/mesoporous hybrid materials composed of metal ions or metal clusters interconnected by organic linkers. MOF-derived metal oxides can inherit abundant pore structures, large surface areas, and active sites in MOF, and feature high electrical conductivity and thermal stability [27,28]. Therefore, MOF-derived electrocatalysts have shown their excellent performance in different electrocatalytic reactions such as oxygen evolution, hydrogen evolution, CO_2 reduction, and nitrogen reduction reactions [29–32]. However, to the best of our knowledge, the application of electrocatalysts with MOFs as sacrificial templates for cathodic reduction remediation has rarely been reported.

Textile white mud is a typical industrial waste generated during the alkali weight-reduction process in printing and dyeing plants, which aims at hydrolyzing the ester bond of terylene (polyethylene terephthalate, PET) using alkali liquor to make the fiber relaxed and light [33]. From the perspective of chemical composition, textile white mud contains a majority of 1,4-dicarboxybenzene, followed by a minority of ethylene glycol, oligomers, and some Fe- or Al-based salts (which are used as reagents for coagulation). Indeed, 1,4-dicarboxybenzene (BDC) is a valuable monomer that meets the required criteria as organic linkers in synthesizing a large number of MOFs (e.g., MIL-88B(Fe), MIL-125(Ti), Co-MOF-74) (Figure 1) [34–36]. Hence, the recovery of 1,4-dicarboxybenzene from textile white mud for fabricating MOFs and their derivatives can mitigate rising textile sludge wastes while developing a cost-effective synthetic process.

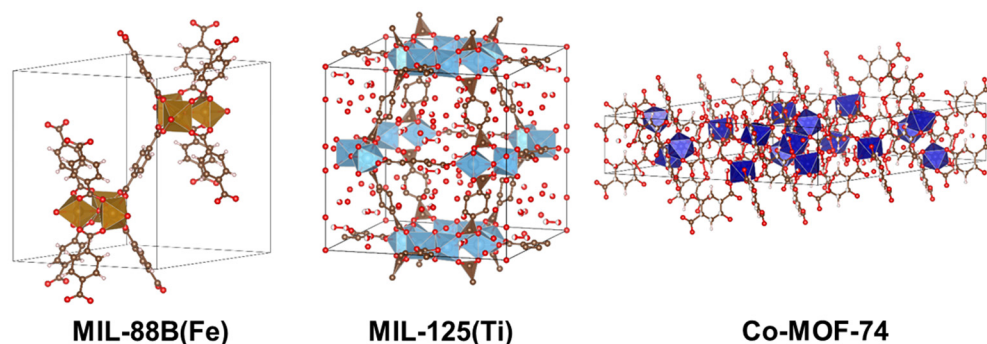


Figure 1. The polyhedral structure of MIL-88B(Fe), MIL-125(Ti), and Co-MOF-74.

Considering the above, we propose a hydrothermal-based roadmap for the separation of 1,4-dicarboxybenzene from textile white mud and the subsequent fabrication of amorphous MIL-125(Ti)-W, along with its derived $\text{TiO}_2\text{@C-W}$. Owing to the abundant heteroatoms brought by the co-existing components for BDC separated from textile white mud, $\text{TiO}_2\text{@C-W}$ derived from MIL-125(Ti)-W is expected to show enriched vacancies and an enhanced surface area. Following this hypothesis, $\text{TiO}_2\text{@C-W}$ is predicted to exhibit satisfactory cathodic reduction activity, according to our previous study [26]. In the later sections, the physicochemical characterization of the fabricated MIL-125(Ti)-W and $\text{TiO}_2\text{@C-W}$, including morphology, crystalline structure, oxygen vacancy, and surface area analysis, is conducted. The effect of water chemistry on FLO removal by $\text{TiO}_2\text{@C-W}$ was investigated. Antibiotics with specific structures including nitrofurazone, metronidazole, and levofloxacin were tested to verify the broad application of $\text{TiO}_2\text{@C-W}$.

2. Materials and Methods

2.1. Textile White Mud and Chemicals

Textile white mud was collected from a printing and dyeing plant located in Jiaying City, China. The wet white mud sample was vacuum-dried at 40 °C, crushed, and screened by an 80-mesh sieve, and stored for further use.

Tetrabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, $\text{Ti}(\text{OBu})_4$, 98%), 1,4-dicarboxybenzene ($\text{C}_8\text{H}_6\text{O}_4$, BDC, 99%), hydrofluoric acid (HF , $\geq 40\%$), sodium borohydride (NaBH_4 , 98%), sodium sulfate (Na_2SO_4 , $\geq 99\%$), sodium chloride (NaCl , $\geq 99.8\%$), sodium bicarbonate (NaHCO_3 , $\geq 99.5\%$), sodium sulfite (Na_2SO_3 , $\geq 97\%$), sulfuric acid (H_2SO_4 , 95~98%), and sodium hydroxide (NaOH , $\geq 96\%$) were obtained by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, DMF, $\geq 99.5\%$) and isopropanol ($\text{C}_3\text{H}_8\text{O}$, $\geq 99.7\%$) were provided by Aladdin Reagent Inc. Florfenicol (FLO, $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{FNO}_4\text{S}$, 98%) was purchased from Shanghai Ruichu Biotech Co., Ltd., Shanghai, China. Methanol (CH_3OH , MeOH, for HPLC, $\geq 99.9\%$) and Nafion[®] solution (5 wt.%) were supplied by Sigma-Aldrich. Toray 090 carbon paper was obtained from the Fuel Cell Store. All aqueous solutions were prepared using Milli-Q DI water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Fabrication of MIL-125(Ti) and $\text{TiO}_2\text{@C}$ Derived from Textile White Mud

Four samples involving MIL-125(Ti) (denoted as MIL-125(Ti)-W) and $\text{TiO}_2\text{@C}$ (denoted as $\text{TiO}_2\text{@C-W}$) derived from textile white mud, and MIL-125(Ti) and $\text{TiO}_2\text{@C}$ derived from BDC chemicals, were fabricated and compared in this study.

The purification and separation of BDC from textile white mud are discussed in detail in Section 3.1. For the fabrication of MIL-125(Ti)-W, 2.492 g of separated BDC was first dissolved in a mixture of 40 mL of DMF and 10 mL of MeOH in a Teflon autoclave with a capacity of 100 mL. The mixture was sonicated for 20 min to ensure the dissolution of BDC. Then 1.3 mL $\text{Ti}(\text{OBu})_4$ was added dropwise with vigorous stirring for 2 h, and the mixture was then maintained at 150 °C for 15 h. After cooling to an ambient temperature, the as-prepared MIL-125(Ti)-W powders were washed and centrifuged by DI water and ethanol

several times and dried at 60 °C overnight. For the derived TiO₂@C-W, 0.5 g MIL-125(Ti)-W was calcined at 350 °C for 1 h in N₂, with the temperature increasing at a rate of 5 °C min^{−1}.

For comparison, MIL-125(Ti) was fabricated using a protocol similar to that used to fabricate MIL-125(Ti)-W, except that the separated BDC was replaced by BDC chemicals. TiO₂@C was derived from MIL-125(Ti).

To prepare the working electrode, all the samples were coated onto carbon papers (20 × 20 mm), as described in Text S1.

2.3. Experimental Setup of Cathodic Reduction Test

A cathodic reduction test was performed in an H-type cell, separated by a Grion 0011 cation-exchange membrane (Figure S1). For a typical process, both compartments were filled with 100 mL of Na₂SO₄ (50 mM) electrolytes, and a target contaminant was added to the catholyte to achieve a certain concentration. Both the working electrode and reference electrode (Ag/AgCl, saturated with 3.0 M KCl solution) were placed into the cathodic chamber, while the counter electrode was placed into the anodic chamber. The cell was controlled by an electrochemical workstation (CHI 650D, Chenhua Co., Shanghai, China) at a constant driving bias. All batch experiments were carried out in triplicate.

2.4. Characterizations and Analytical Methods

Techniques involving X-ray diffraction (XRD, Rigaku Geigerflex with Cu Kα X-ray source), scanning electron microscopy (SEM, Hitachi S-3000N) with an energy dispersive spectrum (EDS), transmission electron microscopy (TEM, JEM-1230 JEOL), Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum Two FT-IR), electron paramagnetic resonance (EPR, Bruker EMXplus X-band), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo scientific, Waltham, MA, USA) were used to characterize the powder samples. Total organic carbon (TOC) was measured using a Shimadzu TOC-L analyzer (Kyoto, Japan).

The concentration of aqueous FLO was measured by a high-performance liquid chromatography (HPLC, LC-20AT, Shimadzu, Tokyo, Japan) equipped with an ODS-SP C18 column (150 × 4.6 mm, filler particles with 5 μm size) and a UV detector at 210 nm. The injection volume was 20 μL. The mobile phase was a mixture of 60% methanol and 40% water (containing 0.5% formic acid) at a constant flow rate of 0.8 mL min^{−1}, and the column temperature was maintained at 30 °C. The calibration curve of the tested compound was determined using the HPLC method. The LOD and LOQ of this HPLC method for FLO were measured using a diluting method, and determined to be 40 μg L^{−1} and 200 μg L^{−1}.

3. Results and Discussion

3.1. Separation of 1,4-Dicarboxybenzene from Textile White Mud

Given that textile white mud consists of not only BDC, but also ethylene glycol, oligomers, and inorganic salts, we first analyzed the elemental components of the dried white mud samples using an elemental analyzer (for C, H, N, and S) and an ICP-OES (for Fe, Si, P, Al, Ca, Mg, Zn, Cr, Cu, and Pb). Despite the main elements like C and H, the content of metal impurities contained in the sample was extremely low, except for Fe and Al, which probably originated from the coagulants used during the precipitation of white mud (Figure 2A). Figure 2B displays a typical SEM image of the sample with its corresponding EDS. Only C and O elements were observed based on the area scan, and the distribution of the O element was even on the solid massive, corresponding to the BDC component.

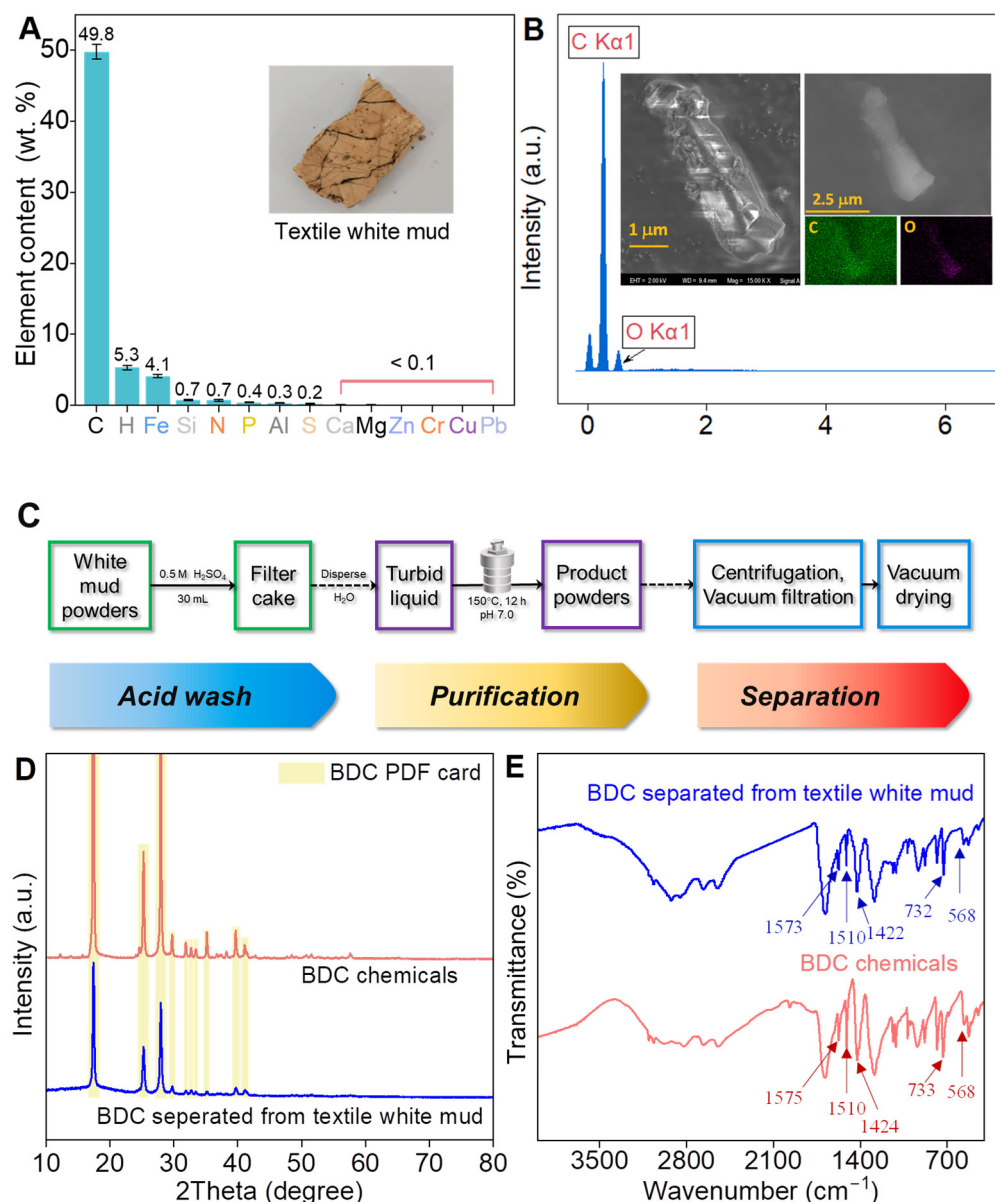


Figure 2. (A) Elemental components of textile white mud; (B) SEM image, dark field image, corresponding EDS spectra, and elemental mapping of textile white mud; (C) scheme of separation of BDC from textile white mud; (D) XRD patterns of BDC separated from textile white mud and BDC chemicals; (E) FTIR spectra of BDC separated from textile white mud and BDC chemicals.

To separate BDC from textile white mud, a multi-step protocol was adopted on the premise of the physicochemical properties of the impurities, as described in Figure 2C. To remove ethylene glycol and soluble inorganic salts (e.g., Fe and Al-based salts), ~10 g of white mud samples was immersed into 0.5 M H₂SO₄, fully mixed, and filtered to obtain the filtered cake. Then, to facilitate the hydrolysis of oligomers and promote the crystallization of BDC, a solvothermal process was conducted by re-dispersing the filtered cake into DI water and the pH adjustment to neutral. Finally, the resulting solid–liquid mixture was centrifuged and separated to obtain purified BDC via vacuum filtration. The yield of BDC was approximately 30%, which was consistent with the measurement by high-performance liquid chromatography for the DMF extraction of white mud samples (30.8%).

To identify the separated BDC, we compared its XRD pattern with that of BDC chemicals. Since all the typical peaks in the BDC standard card (PDF# 31-1916) can be observed on both samples in Figure 2D, the feasibility of the separation protocol was verified. Notably,

the peak intensity for the separated BDC was remarkably lower than that for BDC chemicals, which is probably due to its relatively low crystallinity. Moreover, Figure 2E shows the FTIR spectra of the BDC samples. In the spectrum of BDC chemicals, the absorption bands at 1575 and 1424 cm^{-1} belong to COO antisymmetric and symmetric stretching vibrations, respectively. The bands at 568, 733, and 1510 cm^{-1} were attributed to the vibrations of the phenyl ring [37]. In the spectrum of BDC separated from textile white mud, absorption bands at 1573, 1422, 568, 732, and 1510 cm^{-1} were found. FT-IR spectrum results indicate that the separated BDC powder shows similar characteristic peaks as BDC chemicals do, again confirming the successful separation of BDC from textile white mud.

3.2. Fabrication and Structural Characterization

Subsequently, we performed different characterization techniques on MIL-125(Ti)-W and $\text{TiO}_2\text{@C-W}$ to understand their structural information, with MIL-125(Ti) and $\text{TiO}_2\text{@C}$ as references, respectively. Figure 3 suggests that carbonization significantly affected the morphologies of materials. MIL-125(Ti)-W features a cake-shaped morphology with a particle size of around 1 μm (Figure 3A), similar to MIL-125 (Figure 3D). The only significant difference is that MIL-125(Ti)-W attained a rougher surface, likely due to the residual impurities inherited from textile white mud. After carbonization, the original morphology of MIL-125(Ti)-W was heavily damaged, and $\text{TiO}_2\text{@C-W}$ was mainly composed of incomplete and porous cake-like structures (Figure 3B). On the contrary, $\text{TiO}_2\text{@C}$ maintained maximally the original appearance of MIL-125 (Figure 3E). This observation agrees with the hypothesis that $\text{TiO}_2\text{@C-W}$ may have more structural defects than $\text{TiO}_2\text{@C}$ does, due to the large numbers of heteroatoms coming from the impurities in BDC separated from white mud. The comparison of TEM images shows that $\text{TiO}_2\text{@C-W}$ (Figure 3C) should possess a much higher specific surface area than $\text{TiO}_2\text{@C}$ (Figure 3F) because hollow structures were constructed during the carbonization of MIL-125(Ti)-W.

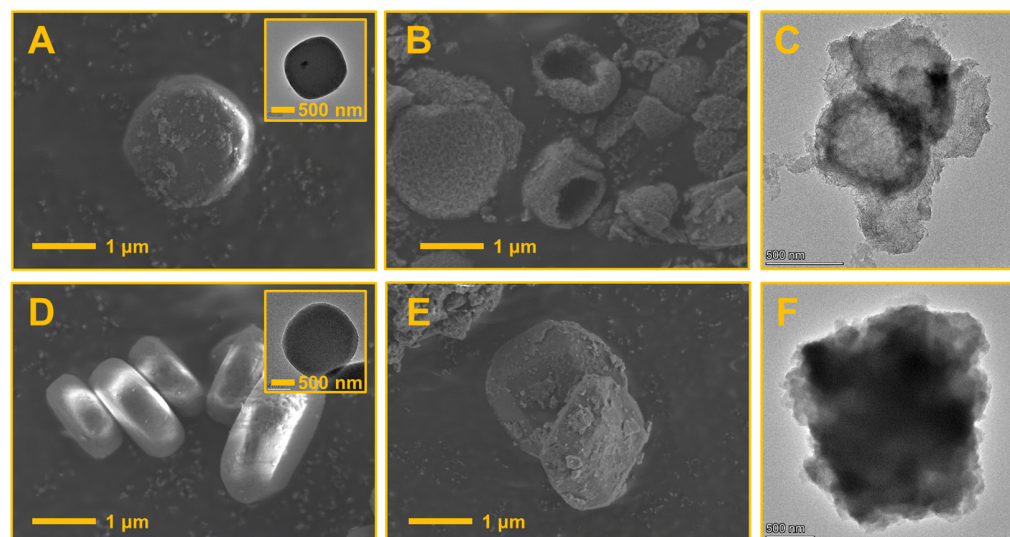


Figure 3. SEM images of (A) MIL-125(Ti)-W (inset: corresponding TEM image) and (B) $\text{TiO}_2\text{@C-W}$; (C) TEM image of $\text{TiO}_2\text{@C-W}$; SEM images of (D) MIL-125(Ti) (inset: corresponding TEM image) and (E) $\text{TiO}_2\text{@C}$; (F) TEM image of $\text{TiO}_2\text{@C}$.

XRD patterns of MIL-125(Ti), MIL-125(Ti)-W, $\text{TiO}_2\text{@C}$, and $\text{TiO}_2\text{@C-W}$ are compared in Figure 4A. The pattern of MIL-125(Ti) fabricated from BDC chemicals was in good accordance with the simulated XRD from the cif-file of CCDC 220475 (the crystallographic data for MIL-125(Ti)) [38]. The main peaks were assigned to the (011), (002), and (121) planes [39]. No sharp peak was found on that of MIL-125(Ti)-W, suggesting that MIL-125(Ti) was present in a highly crystalline state, while MIL-125(Ti)-W was amorphous. After carbonization, both $\text{TiO}_2\text{@C-W}$ and $\text{TiO}_2\text{@C}$ appeared as amorphous forms, suggesting the

highly disordered atom arrangement. The building of surface oxygen vacancies (OVs) over the TiO_2 catalyst was deemed to increase the electric conductivity and reduce the charge transfer resistance, thus resulting in good electrocatalytic activity [40]. The OVs of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$ were characterized by EPR. As shown in Figure 4B, the field signal at $g = 2.003$ can be attributed to the defects related to oxygen vacancies [41]. Notably, $\text{TiO}_2@\text{C-W}$ displayed stronger signals than those of $\text{TiO}_2@\text{C}$, indicating a far higher OV content of $\text{TiO}_2@\text{C-W}$, though both $\text{TiO}_2@\text{C-W}$ and $\text{TiO}_2@\text{C}$ are disorganized solids. To clarify the state of Ti on the $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$ electrodes, a high-resolution XPS of Ti 2p was measured and is illustrated in Figure 4C. The Ti element had two valence states: In the XPS of the Ti2p spectrum of $\text{TiO}_2@\text{C}$, peaks at a high-binding energy of 458.7 and 465.4 eV were assigned to $\text{Ti}^{4+}2p_{3/2}$ and $\text{Ti}^{4+}2p_{1/2}$, respectively, and the two peaks at 460.3 and 464.3 eV were ascribed to the binding energy of $\text{Ti}^{3+}2p_{3/2}$ and $\text{Ti}^{3+}2p_{1/2}$, respectively. Peaks at a high binding energy of 458.5, 465.2, 459.7, and 464.1 eV were assigned to $\text{Ti}^{4+}2p_{3/2}$, $\text{Ti}^{4+}2p_{1/2}$, $\text{Ti}^{3+}2p_{3/2}$, and $\text{Ti}^{3+}2p_{1/2}$, respectively, in that of $\text{TiO}_2@\text{C-W}$. The $\text{Ti}^{3+}/\text{Ti}^{4+}$ molar ratio of $\text{TiO}_2@\text{C-W}$ (2.0) was significantly higher than that of $\text{TiO}_2@\text{C}$ (0.6). The specific surface area of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$ was determined using a specific surface area analyzer by means of the nitrogen adsorption–desorption isotherm method, calculated with the Brunauer–Emmet–Teller equation. As shown in Figure 4D, the specific surface area of $\text{TiO}_2@\text{C-W}$ was $247.8 \text{ m}^2\text{g}^{-1}$, which was 25-fold that of $\text{TiO}_2@\text{C}$ ($9.9 \text{ m}^2\text{g}^{-1}$). Collectively, the much-enhanced oxygen vacancy content and specific surface area suggest the elevated cathodic reduction performance of $\text{TiO}_2@\text{C-W}$.

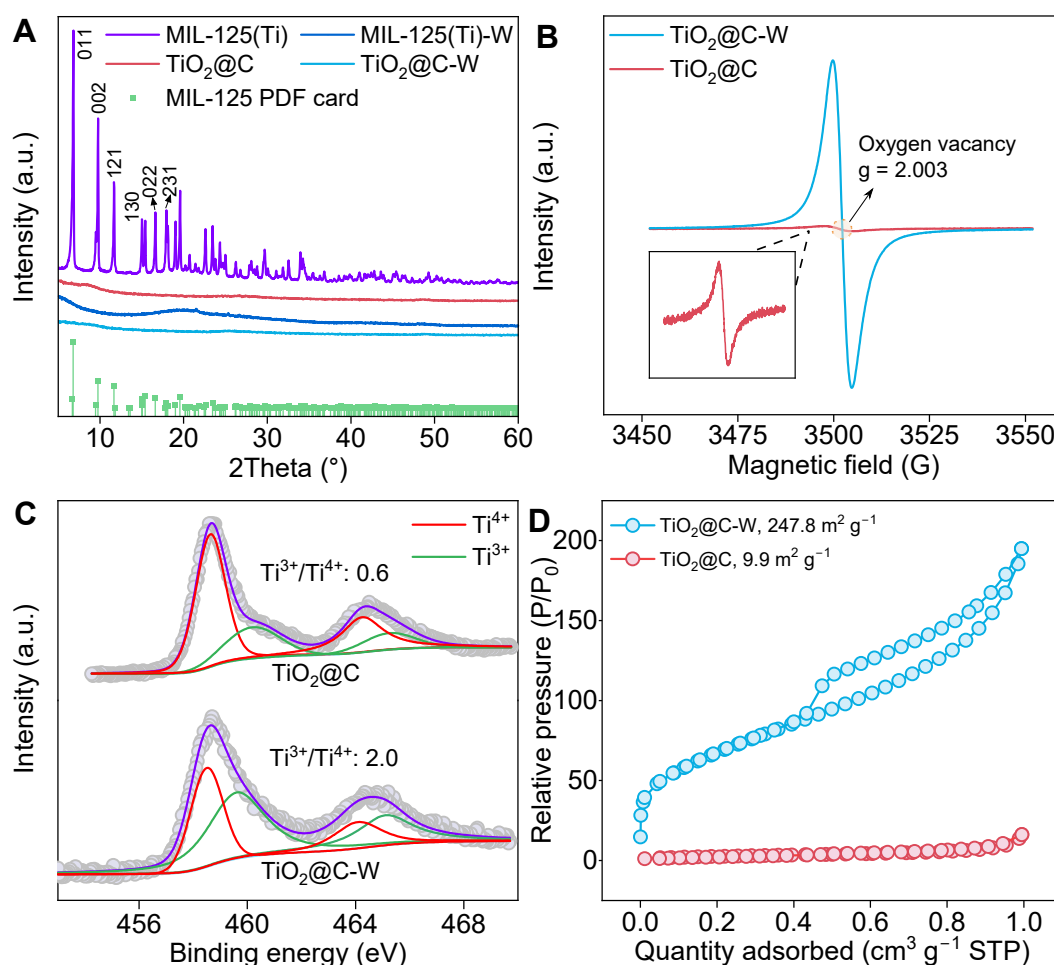


Figure 4. (A) XRD patterns of MIL-125(Ti), MIL-125(Ti)-W, $\text{TiO}_2@\text{C}$, and $\text{TiO}_2@\text{C-W}$; (B) EPR spectra of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$; (C) Ti 2p XPS of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$; (D) N_2 adsorption–desorption isotherm of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C-W}$.

3.3. Cathodic Reduction Performance of TiO₂@C-W

Before evaluating TiO₂@C-W, it was essential to distinguish between the contribution of cathodic reduction and electro-Fenton (refers to the selective electrocatalytic reduction of O₂ to reactive oxygen species) in this system, because the abundant carbonaceous components in TiO₂@C-W may be conducive to an oxygen reduction reaction (ORR). Figure S2 compares the cathodic reduction test of FLO under different atmospheres. Note that the continuous influx of O₂ greatly inhibits the FLO removal, and the exclusion of O₂ by N₂ purging can somehow benefit this process. The participation of ORR was limited in this case. This was probably because the working potential window of the ORR pathway was far from −1.2 V vs. Ag/AgCl.

Secondly, the role of adsorption in FLO removal was addressed by performing a pre-adsorption test without bias. As illustrated in Figure S3, the reduction of FLO by adsorption over different electrocatalysts can be neglected, though the carbonaceous component was included in TiO₂@C-W and TiO₂@C.

To compare the reaction rate of FLO by different electrocatalysts, the removal kinetic data were described with the classical pseudo-first-order model:

$$\ln(C_t/C_0) = -k_{\text{obs}} \cdot t \quad (1)$$

where C_t (mg L^{−1}) and C_0 (mg L^{−1}) are the concentrations of FLO at t and 0 min, and k_{obs} (min^{−1}) refers to the observed rate constant.

3.3.1. Screening of BDC:Ti Molar Ratio and Carbonization Temperature

To determine the optimum fabrication protocol for TiO₂@C-W, we sequentially investigated the molar ratio of BDC to Ti during the preparation of the MIL-125(Ti)-W template and the carbonization temperature during the preparation of the derived TiO₂@C-W.

As shown in Figure S4A, the FLO reduction efficiency of TiO₂@C-W at 180 min achieved 78.4%, with a BDC:Ti molar ratio of 3:0.5. With the decrease of the BDC:Ti molar ratio to 3:1, the FLO reduction efficiency could be elevated to 95.2%. Interestingly, a further decrease in BDC:Ti failed to further increase the performance of TiO₂@C-W for FLO reduction. Figure S4B illustrates this phenomenon. Indeed, the BDC:Ti molar ratio during MIL-125(Ti) fabrication was always set as 3:1 in most of the reports [42–44]. If the 3:1 molar ratio was enough to construct the framework structure of MIL-125(Ti)-W, then a BDC:Ti molar ratio less than 3:1 may result in a mixture of MIL-125(Ti)-W and an unbound BDC ligand. However, the carbonization process may decompose the unbound BDC, which is probably why the batches with a decreased BDC:Ti molar ratio showed neglected differences for FLO reduction. In contrast, the 3:0.5 molar ratio would lead to a mixture of MIL-125(Ti)-W and extra-hydrolyzed Ti(OH)₄ gels. After carbonization, the as-prepared mixture of TiO₂@C-W and TiO₂ exhibited a poorer performance for FLO reduction than TiO₂@C-W alone did. Hence, the BDC:Ti molar ratio of 3:1 enabled good FLO reduction and thus was selected as the appropriate proportion.

The carbonization temperature may simultaneously affect the decomposition extent of MIL-125(Ti)-W and the physicochemical properties of the derived TiO₂@C-W. The decomposition temperature of MIL-125(Ti) was reported to be around 350 °C. As shown in Figure S5A,B, the incomplete carbonization temperature (200 °C) would reduce the catalytic activity of TiO₂@C-W, while the further increased carbonization temperature (400 °C) showed almost no impact.

3.3.2. Comparison with Other Electrocatalysts

The performance of TiO₂@C-W was compared with that of several reference and benchmark electrocatalysts including TiO₂@C derived from MIL-125(Ti) fabricated by reagents, pristine TiO₂, oxygen vacancy-engineered TiO₂ as reported in our previous study (TiO_{2−x}) [26], and commercial Pd(3 wt.%)/C. Figure 5A indicates that TiO₂@C-W showed similar catalytic activity for FLO reduction as Pd(3 wt.%)/C did, which was substantially

higher than that of TiO_{2-x} , TiO_2 , and $\text{TiO}_2@\text{C}$. Figure 5B further quantifies the reaction rate for FLO reduction, which followed an order of $\text{Pd}(3 \text{ wt.}\%)/\text{C}$ (0.018 min^{-1}) $\sim$ $\text{TiO}_2@\text{C}-\text{W}$ (0.017 min^{-1}) $>$ TiO_{2-x} (0.012 min^{-1}) $>$ TiO_2 (0.009 min^{-1}) $>$ $\text{TiO}_2@\text{C}$ (0.005 min^{-1}). The high activity of $\text{TiO}_2@\text{C}-\text{W}$ corresponded to its abundant oxygen vacancies (Figure 4B) and large surface area (Figure 4D). This result suggests that $\text{TiO}_2@\text{C}-\text{W}$ is a promising electrocatalyst for cathodic reductive remediation.

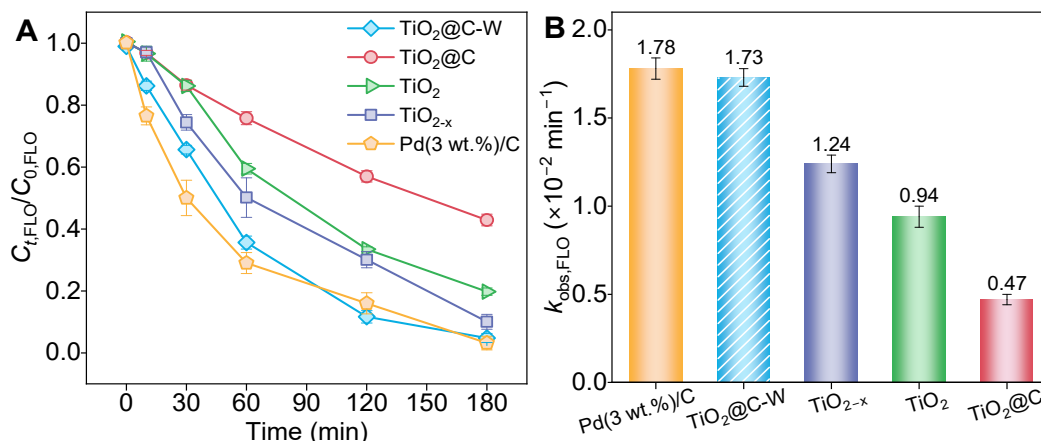


Figure 5. (A) C_t/C_0 and (B) pseudo-first-order kinetic rate constants for FLO reduction by $\text{TiO}_2@\text{C}-\text{W}$, $\text{TiO}_2@\text{C}$, TiO_2 , TiO_{2-x} , and $\text{Pd}(3 \text{ wt.}\%)/\text{C}$ (reaction conditions: $[\text{FLO}]_0 = 20 \text{ mg L}^{-1}$, applied bias = -1.2 V , $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$).

In addition, we tested the reusability of $\text{TiO}_2@\text{C}-\text{W}$ by performing eight consecutive runs, with $\text{TiO}_2@\text{C}$ as a reference. Figure 6 suggests that although the activity of $\text{TiO}_2@\text{C}-\text{W}$ underwent a decrease with the increasing number of runs, it was still more reactive than that of $\text{TiO}_2@\text{C}$. The gradual decreasing activity of $\text{TiO}_2@\text{C}-\text{W}$ is likely to be attributed to the partial detachment of powder catalysts from the electrode. Fortunately, the downward trend of activity was alleviated in the final five runs, suggesting that the mechanical stability of $\text{TiO}_2@\text{C}-\text{W}$ was acceptable.

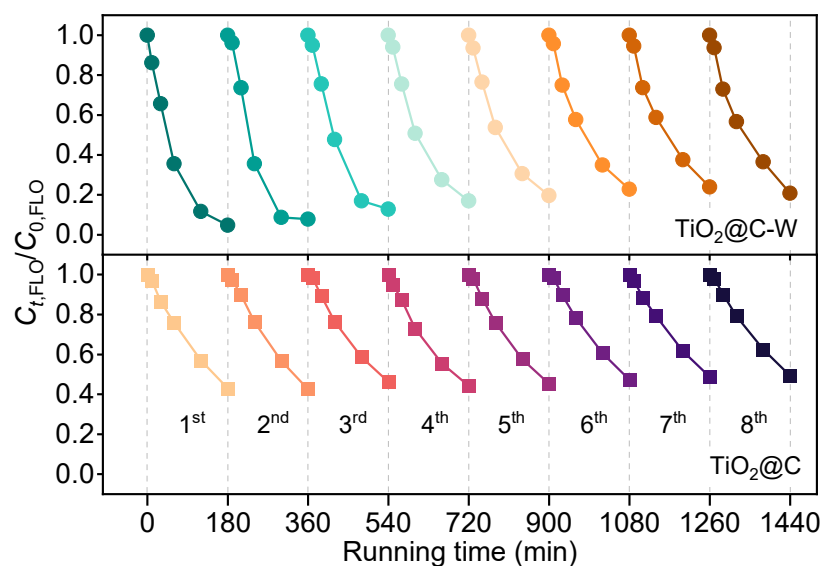


Figure 6. Evolution of $C_{t,\text{FLO}}/C_{0,\text{FLO}}$ in each run during a consecutive 8-run reusability test of $\text{TiO}_2@\text{C}$ and $\text{TiO}_2@\text{C}-\text{W}$, (reaction conditions: $[\text{FLO}]_0 = 20 \text{ mg L}^{-1}$, applied bias = -1.2 V , $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$).

3.4. Effect of Solution pH and Co-Existing Ions on Performance of TiO₂@C-W

The effect of the solution pH was also studied because it always plays an important role in electrocatalytic reductive dehalogenation reactions [45,46]. Figure 7A presents the cathodic reduction of FLO by TiO₂@C-W as a function of time under acidic (pH 3.9), weak acidic (pH 5.6), neutral (pH 7.1), and basic (pH 9.7) conditions, suggesting that TiO₂@C-W showed FLO reduction efficiency (95.2%, 180 min) at acidic conditions, which was substantially higher than that at weak acidic (74.1%), neutral (63.0%), and basic conditions (59.9%). These data were fitted with Equation (1). Figure 7B shows that $k_{\text{obs, FLO}}$ (0.017 min^{−1}) of TiO₂@C-W for FLO reduction was 2.2, 3.0, and 3.3 times higher than that at weak acidic, neutral, and basic conditions, respectively. Indeed, our previous study suggests that the solution could significantly affect the reductive degradation of FLO, mainly because (I) sufficient H⁺ in the solution could boost the proton transfer during dehalogenation and thus enhance the reaction rate, and (II) overdosed H⁺ in the solution may inhibit FLO reduction by accelerating the hydrogen evolution reaction (HER) as a side reaction [47]. Since the oxygen vacancy-engineered molecular-imprinted TiO₂ prepared in our previous study showed an obvious activity decline when the initial solution pH is lower than 4.0, TiO₂@C-W proposed in this study may own a wider pH working range.

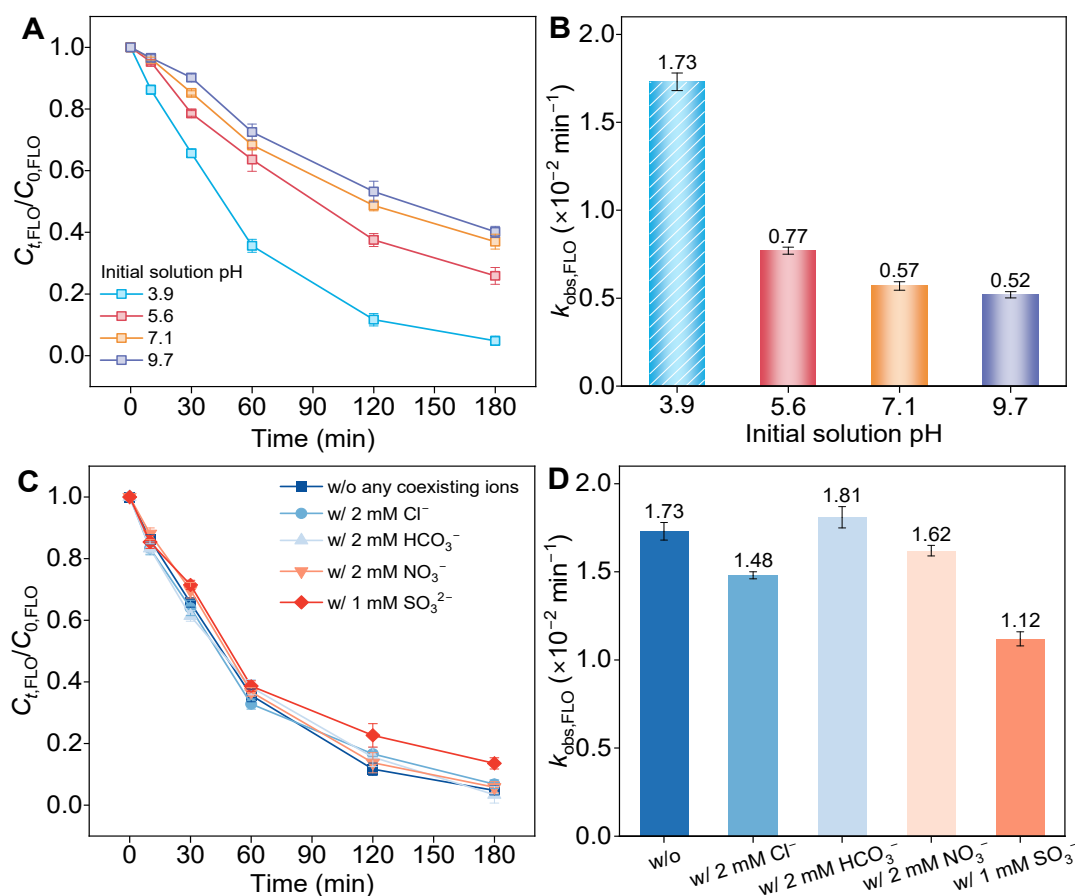


Figure 7. Effect of initial solution pH on (A) reduction efficiency ($C_{t,\text{FLO}}/C_{0,\text{FLO}}$) and (B) pseudo-first-order kinetic rate constants $k_{\text{obs, FLO}}$ by TiO₂@C-W; effect of co-existing anions on (C) reduction efficiency ($C_{t,\text{FLO}}/C_{0,\text{FLO}}$) and (D) pseudo-first-order kinetic rate constants $k_{\text{obs, FLO}}$ by TiO₂@C-W (reaction conditions: [FLO]₀ = 20 mg L^{−1}, applied bias = −1.2 V, [Na₂SO₄] = 50 mM).

Water chemistry can also affect the cathodic reduction of pollutants, because the co-existing ions may adsorb onto the active sites, therefore preventing the pollutants from moving closer to the surface of the electrode. For instance, the presence of co-existing anions such as Cl[−], NO₃[−], and HCO₃[−] has been proven to disturb the catalytic activity of

Pd-based cathodes [48]. To elucidate the effect of typical co-existing anions on the reduction of FLO by $\text{TiO}_2\text{@C-W}$, we repeated the cathodic reduction test in the presence of 2 mM Cl^- , 2 mM HCO_3^- , 2 mM NO_3^- , and 1 mM SO_3^{2-} , respectively. Figure 7C suggests that all the selected anions show negligible negative impacts on FLO reduction. Figure 7D confirms the result and the slightly decreased $k_{\text{obs, FLO}}$ may be attributed to the fact that the presence of co-existing anions increases the ionic conductivity of the electrolyte and thereby accelerates the HER side reaction [49].

3.5. Cathodic Reduction Performance for Other Antibiotics by $\text{TiO}_2\text{@C-W}$

We also tested the cathodic reduction performance of $\text{TiO}_2\text{@C-W}$ for other antibiotic contaminants with specific structures including nitrofurazone (NFZ), metronidazole (MNZ), and levofloxacin (LFX). NFZ contains a nitro group and a furan ring in its molecular structure. MNZ features a nitro group and an imidazole ring. LFX is one of the third-generation quinolone antibiotics, containing a fluorine atom in its structure. As shown in Figure 8A, approximately 95% NFZ and 93% MNZ can be removed at 180 min, while the removal efficiency for LFX is relatively low (~68%). Further analysis based on the pseudo-first-order kinetic model indicates that the k_{obs} value of these contaminants follows an order of NFZ (0.019 min^{-1}) > FLO (0.017 min^{-1}) > MNZ (0.015 min^{-1}) > LFX (0.007 min^{-1}) (Figure 8B), which is presumably due to their various moieties. Kong et al. [18] conducted cyclic voltammetry to study the electro-reductive behavior of a series of antibiotics, and found that NFZ is more easily reduced than that of MNZ and FLO. The reduction in $\text{TiO}_2\text{@C-W}$ shows a higher removal efficiency and k_{obs} of the degradation of MNZ, NFZ, and LFX compared with reductions in the previous reports. Furthermore, the toxicity assessment of cathodic reduction degradation products of NFZ and MNZ to selected bacterial strains by Deyong Kong and his co-workers revealed the reduced toxicity of degradation products compared to the parent antibiotics [18]. Generally, the dehalogenation reaction makes halogenated and nitro group reduction compounds less toxic and more readily biodegradable as the addition [50,51].

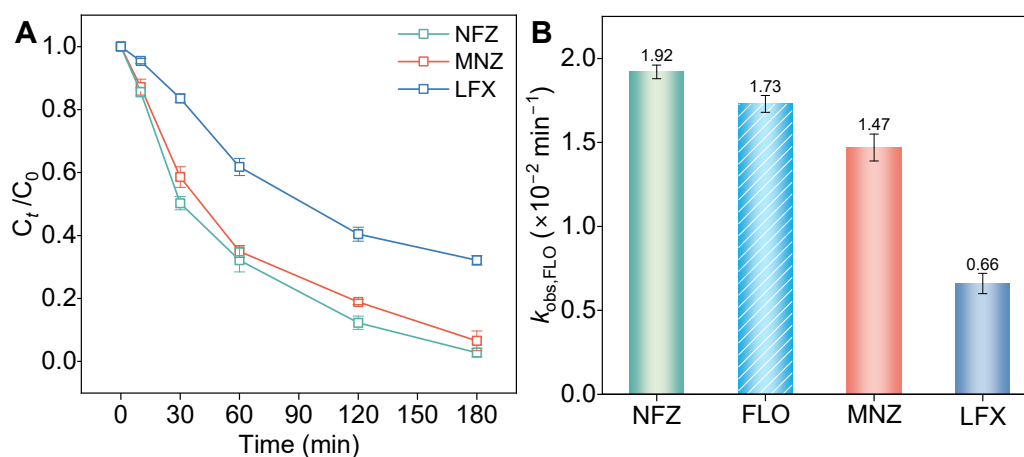


Figure 8. (A) C_t/C_0 and (B) pseudo-first-order kinetic rate constants for nitrofurazone (NFZ), metronidazole (MNZ) and levofloxacin (LFX) removal by $\text{TiO}_2\text{@C-W}$ (reaction conditions: $[\text{NFZ}]_0 = [\text{MNZ}]_0 = [\text{FLO}]_0 = 20 \text{ mg L}^{-1}$, applied bias = -1.2 V , $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$).

The total organic carbon (TOC) removal of four antibiotics by $\text{TiO}_2\text{@C-W}$ was investigated. As shown in Figure S6, the TOC removal percentages of FLO and LFX after 2 h were 7% and 15%, respectively, suggesting the two antibiotics were degraded mainly through a reduction pathway along with a slight oxidation reaction. The pathway of the cathodic degradation of NFZ was proposed (Figure S7). The main reaction was the nitro group reduction, and the C-N unsaturated bond and N-N bond were also attacked. Specifically, the cleavage of the N-N bond resulted in the split of a moiety containing organic carbon. Finally, the amine-containing furan ring was degraded to generate two linear chain prod-

ucts. The high TOC removal percentages of the NFZ (48%) could both be attributed to the cleavage of the N-N bond, and the electro-Fenton oxidation (mineralization). Compared to the NFZ degradation, only the nitro group reduction occurred during the MNZ cathodic reduction. A moderate TOC removal (54%) of MNZ was mainly attributed to the electro-Fenton oxidation. The reductive degradation of LFX by $\text{TiO}_2\text{@C-W}$ was out of expectations because LFX degradation is well-known for the oxidation pathway [52], while the less common reduction pathway (e.g., defluorination) requires noble metals [53]. The degradation pathway of LFX in this system will be reported in a follow-up study that is underway.

4. Conclusions

Developing cost-effective, high-performance electrocatalysts is one of the keys to tackling the challenge while promoting the popularization of cathodic remediation. In this study, we propose a novel strategy for upcycling textile white mud, a typical waste from the printing and dyeing industry, to fabricate amorphous $\text{TiO}_2\text{@C}$ for highly efficient cathodic reduction. $\text{TiO}_2\text{@C-W}$ fabricated from separated BDC from white mud features displays a higher degree of oxygen vacancies and a 25-fold higher specific surface area than that of $\text{TiO}_2\text{@C}$ derived from BDC chemicals. $\text{TiO}_2\text{@C-W}$ shares similar cathodic reductive activity as commercial $\text{Pd}(3 \text{ wt.}\%)/\text{C}$ to antibiotic florfenicol (FLO), and shows acceptable mechanical stability. A lower initial solution pH boosts the cathodic reduction process, while common co-existing anions show limited negative impact. Finally, $\text{TiO}_2\text{@C-W}$ shows reductive activity for several representative antibiotics. The findings from this study obey the “waste control by waste” approach and furnish further directives for the design of electrocatalysts for electro-reductive remediation. The cathode material $\text{TiO}_2\text{@C-W}$ with high reduction efficiency could be potentially applied to the pretreatment of various antibiotics before the biodegradation approach, and the separation of BDC from textile white mud provides a cost-effective raw material for the fabrication of other MOFs (e.g., MIL-88B(Fe), Co-MOF-74). Furthermore, the species of impurities in the separated BDC from white mud and the impacts on $\text{TiO}_2\text{@C}$ could be studied in more depth in future research.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations10120580/s1>, Text S1. Working electrode preparation. Figure S1: H-type cell for cathodic reduction test. Figure S2: Cathodic reduction test of FLO under different atmospheres. Figure S3: Adsorption of FLO by different electrocatalysts. Figures S4–S5: Effect of molar ratio of BDC:Ti and temperature calcination on the electro-reductive degradation efficiency of FLO. Figure S6: Evolution of solution TOC removal (as mineralization efficiency) as a function of treatment time in cathodic reduction process for florfenicol (FLO), nitrofurazone (NFZ), metronidazole (MNZ) and levofloxacin (LFX) removal by $\text{TiO}_2\text{@C-W}$. Figure S7: Proposed pathways of the cathodic degradation of nitrofurazone (NFZ) and metronidazole (MNZ). Table S1: Comparison of removal efficiency and k_{obs} with the previous reports. Refs. [54–61] are cited in Supplementary Materials.

Author Contributions: J.Z.: conceptualization, methodology, data curation. X.W.: data curation, formal analysis. Y.F.: validation, investigation. S.R.: software, formal analysis. Z.L.: conceptualization, investigation, funding acquisition, writing—original draft. J.L.: supervision, funding acquisition, writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of the study are available from the corresponding author upon request.

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

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