Determinant of chemical oxygen demand in mixed organic solution by Ti/TiO2 nanotube array electrode method

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ABSTRACT

Chemical oxygen demand (COD) is a significant parameter for analyzing water quality. However, the detection methods still suffer from the problems of secondary pollution, use of harmful substances, complicated operations, etc. To trace these problems, a Ti/TiO2 nanotube array (NTA) electrode was successfully prepared by the secondary anodic oxidation method in this work. The prepared electrode was used to determine COD of single- and multi-component solutions (including aniline, rhodamine B, and potassium hydrogen phthalate). The Ti/TiO2 NTA electrode exhibited higher electrochemical oxidation efficiency than the neat Ti one. The electrocatalytic reactions of the target organics on the electrode surface were confirmed to conform to the first-order kinetic process. Within COD range of 5–150 mg/L, COD value was not only proportional to the anodizing current but also related to organic matter itself. The activation energies of electro-oxidation reaction of different substances were different from each other (An: 14.25 kJ/mol, RhB: 18.56 kJ/mol, and KHP: 35.32 kJ/mol), indicating the differences in their dynamic behaviors on the electrode surface. The related bias obtained for all successive measurements was below ± 5.8%. Therefore, we report a fast, effective, accurate, and well-reproducible COD detection method, which is feasible for both single-component and multiple-component organic solutions.

Key words: chemical oxygen demand, electrochemical method, multi-component solution, Ti/TiO2 electrode

HIGHLIGHTS

\begin{itemize}
  \item A Ti/TiO2 nanotube array electrode was prepared by the secondary anodic oxidation method, a simple and rapid way.
  \item The Ti/TiO2 electrode exhibited high electrochemical performance. Its electro-oxidation kinetics conformed to the first-order kinetics.
  \item For COD determination by the Ti/TiO2 electrode, net current was affected by temperature, types, and ratios of organics, due to functional groups of the organics.
\end{itemize}

GRAPHICAL ABSTRACT

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1. INTRODUCTION

The increasing water pollution has become one of the pressing global challenges, which makes environmental monitoring and control a global concern (Shannon et al. 2008; Eruc & Hoekstra 2014; UNESCO & UN-Water 2020). Chemical oxygen demand (COD) reflects the degree of contamination of water by reducing substances and is one of the most widely used indicators in the field of water-quality analysis such as wastewater effluent monitoring and taxation of wastewater pollution, etc. (Zheng et al. 2008). The potassium dichromate method, as the traditional COD method, is applied to evaluate the demand of oxygen required for the oxidative degradation of organic compounds. The conventional process of this method includes the complicated operation steps of catalytic oxidation, reflux, and titration. It requires 2–4 hours of operation time to achieve sufficient oxidation for COD determination, so it is difficult to apply for online monitoring or on-site evaluation (Li et al. 2006b; Ge et al. 2016). Besides, it also consumes some corrosive, expensive, and toxic chemicals such as H₂SO₄, Ag₂SO₄, Hg²⁺, and Cr₂O₃⁻, leading to secondary pollution and high cost (Silva et al. 2009; Ge et al. 2016).

In the past years, significant advances have been made for the accurate determination of COD values. However, a formidable challenge is still not solved comprehensively to develop a precise, rapid, and environmentally benign method for COD determination. Electrode technology measurement methods have been developed through electrocatalytic approaches using electrodes such as PbO₂ (Ai et al. 2004; Mo et al. 2015), Cu (Silva et al. 2009; Carchi et al. 2019), Ti (Ge et al. 2016), etc., to shorten the analysis time. Mo et al. reported a three-dimensional structured β-PbO₂-coated crisscrossing carbon fiber electrode for measuring COD values in wastewater (Mo et al. 2015). This electrode possessed a wide linear range of COD values (50–5,000 mg/L), high sensitivity, excellent reproducibility, and low cost. But this method was limited by the highly toxic heavy metal lead. Silva et al. demonstrated the feasibility of an electrochemical method using Cu electrodes to determine COD (Silva et al. 2009). In addition to low cost and simple preparation, the electrode has good stability for up to 15 days. However, the measurement time of 10–20 min was still not short enough and limited the development of this method. Besides, Carchi et al. prepared Cu/CuONf electrodes by covering Cu/CuO electrodes with Nafion (NF) film (Carchi et al. 2019). The improved electrode measures the COD value more accurately and has a longer lifetime than the original Cu/CuO one, but the sensitivity is reduced by about 15%. Compared with these methods, electrocatalytic approaches using Ti/TiO₂ electrodes are more promising because of the superior oxidative abilities of TiO₂ and the short time required for analysis (Cheshideh & Nasirpouri 2017; Ramasundaram et al. 2017; Yi et al. 2019; Chen et al. 2020c). Moreover, TiO₂ nanomaterials are inexpensive, non-toxic, and environmentally friendly, and therefore have recently attracted interest in improving the catalytic degradation of various organic substances (Song et al. 2020). The main disadvantage of the Ti/TiO₂ electrode method in actual COD determination is that the electron/hole pairs generated in the discrete TiO₂ nanoparticles and the coated nanofilms are easy to recombine, resulting in low catalytic activity. It means a narrow dynamic working range and relatively poor reproducibility. For the COD determination using the electrochemical technique of Ti, Ge et al. developed a Ti/TiO₂ electrode by anodizing method (Ge et al. 2016). The rapidity and accuracy of this method for monitoring COD values were confirmed. However, this study lacks research on diversified target solutions and only tested two single-component solutions of potassium hydrogen phthalate and phenol. Therefore, the research and analysis of Ti/TiO₂ electrode kinetics, the detection of diversified target solutions, and the development of electrodes are still of substantial value and far-reaching scientific significance within the working range of 5–150 mg/L COD value.

To deeply study the research, we had prepared a Ti/TiO₂ electrode with nanotube array (NTA) structure by the secondary anodic oxidation method. The preparation and characterization of the prepared electrode, the electrolysis kinetics of different organic substances on the electrode surface, and their application in COD determination of single- and multi-component mixed organic solutions are described in detail below.

2. MATERIALS AND METHODS

2.1. Experimental device

The experimental device consisted of an electrochemical workstation, a magnetic stirrer, an electrolytic cell, a working electrode, a counter electrode, and a reference electrode (Wang et al. 2020). The schematic diagram of the three-electrode system device is shown in Figure 1. In this work, the electrochemical workstation provided a stable current output. A prepared Ti/TiO₂ NTA electrode was used as the working electrode, and the area of the electrode immersed in the electrolyte is 100 mm². A Pt electrode or a porous graphite electrode was used as the counter electrode. The electrode spacing between the Ti/TiO₂ NTA electrode and the counter electrode is 2.5 cm. A saturated calomel electrode (SCE) was used as the
reference electrode. Besides, a 0.1 mol/L Na₂SO₄ solution, as the supporting electrolyte, was stirred constantly in the electrolytic cell. However, for the electrochemical experiments, the final electrolyte was prepared by adding organic solutions into the supporting electrolyte (Chen et al. 2020b).

2.2. Materials
Titanium sheet (Ti sheet, 99.99% purity), nitric acid (HNO₃), hydrochloric acid (HCl), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄, 98 wt%), aniline (An), and potassium hydrogen phthalate (KHP) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Ethylene glycol (EG) and ammonium fluoride (NH₄F) were brought from Shenyang Xinxing Reagent Factory, Shenyang, China. Hydrofluoric acid (HF) was from Shenyang Chemical Reagent Factory, Shenyang, China. Moreover, acetone, anhydrous ethanol, sodium sulfate (Na₂SO₄), and rhodamine B (RHB) were purchased from Damao Chemical Reagent Factory, Tianjin, China. For all purposes, Millipore water was applied.

2.3. Preparation of a Ti/TiO₂ NTA electrode
In this work, the Ti/TiO₂ NTA electrode was prepared by the secondary anodic oxidation method (Figure 2). A pure Ti sheet with a size of 15 mm × 60 mm × 0.4 mm was polished with 800, 1000, and 2000 grit abrasive paper to obtain a flat surface, and ultrasonically cleaned with acetone for 30 min, anhydrous ethanol for 15 min, and distilled water for 15 min, respectively. After that, the Ti sheet was etched with HF/HNO₃/H₂O solution (volume ratio = 1:2:5) for 20 s, and then dried at 80 °C.

Next, TiO₂ NTA was prepared on the surface of the Ti sheet by the twice anodization process. The pretreated Ti sheet was firstly anodized at 60 V for 30 min in EG electrolyte containing NH₄F (0.5 wt.%) and H₂O (5 vol.%), and a Pt electrode was used as the cathode. The oxide film formed on the surface was removed by ultrasonication in HCl (1 mol/L) for 5 min and

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**Figure 1** | Schematic depiction of the three-electrode system device.

**Figure 2** | Schematic diagram of the formation mechanism of Ti/TiO₂ NTA electrode prepared by anodic oxidation method (Tao & Tao 2008; Chen et al. 2020a).
then in absolute ethanol for 3 min. The as-prepared sheet was calcined without oxygen at 600 °C for 1 h. Then, the second anodization was performed for 1 h under the same condition as the first one. The sample was then rinsed with HCl (1 mol/L) for 3 min and then washed with acetone, absolute ethanol, and distilled water in order. Finally, the fabricated Ti/TiO$_2$ NTA electrode was calcined in a muffle furnace at 450 °C for 2 h (Tao & Tao 2008; Chen et al. 2020a).

2.4. Instrumental characterization

The structure and morphology of the Ti/TiO$_2$ NTA electrode were characterized by a field emission scanning electron microscopy (FE-SEM, SU8010, Hitachi Co., Tokyo). The crystal phase of the Ti/TiO$_2$ NTA was conducted via X-ray diffraction (XRD, Empyrean, PANalytical Co., Netherlands), operating at 40 kV/40 mA using Cu-K$_\alpha$ radiation. In addition, linear scanning voltammetry (LSV) was used in electrochemical tests to measure the oxygen evolution potential of the electrode with 0.1 mol/L Na$_2$SO$_4$ electrolytes. The sweep speed was performed at 50 mV/s in the sweep voltage range from 0.0 to 3.0 V. A double beam ultraviolet-visible spectrophotometer (UV-vis, TU-1901, Beijing Puxi General Instrument Co., Ltd, China.) was used to analyze the solution absorbance.

2.5. Electrochemical measurement

For the electrode reaction kinetics, the three-electrode system device was applied for the experiments of electrocatalytic degradation (Figure 1). A porous graphite electrode was used as the counter electrode. The solutions of target organics, such as An, RhB, and KHP, were respectively added into the supporting electrolyte to obtain the final COD value of 50 mg/L (Chen et al. 2020b). The target organic solutions respectively degraded at different temperatures from 298 to 328 K. The degradation solutions were measured at the reaction time of 0–180 min. Using the UV-vis, the absorbance of An, RhB, and KHP were analyzed at the wavelength of 479 nm, 230 nm, and 270 nm, respectively. Furthermore, the degradation rate (η) of the target degradation product at any time (t) can be obtained by the following formula:

$$\eta (\%) = \frac{A_0 - A_t}{A_0}$$

Among them, $A_0$ is the initial absorbance of the target organic solution, and $A_t$ is the absorbance of the target degradation product at a degradation time $t$ (Chen et al. 2020c; Zhang et al. 2020).

For the COD determination experiments, the same three-electrode system was used (Figure 1); the preparation method of the electrolyte was to add a standard solution with a known COD value to a 0.1 mol/L Na$_2$SO$_4$ solution. The working electrode voltage was controlled at 2–3.5 V (vs. SEC). The current was read after 60 s for stabilization. Compared with the conventional COD method, the Ti/TiO$_2$ electrode method has the advantages of short analysis time, low cost, non-toxicity, and environmental friendliness.

3. RESULTS AND DISCUSSION

3.1. Morphology characterization

Figure 3 shows an SEM image of the Ti/TiO$_2$ electrode surface with nanotube array structure. The three-dimension TiO$_2$ nanotube array was prepared on a Ti sheet by the secondary electrochemical anodization. From the SEM image, the surface of the electrode is composed of a large number of ordered nanotubes, and the diameter of the inner hole is ~100 nm. The uniform TiO$_2$ nanotubes are high-ordered in structure, well-aligned with each other through the walls of the TiO$_2$ nanocrystalline tubes, and perpendicular to electrically conductive Ti substrates, thereby naturally forming a Schottky-type contact (Liu et al. 2009). Thus, due to the high surface area of TiO$_2$ NTA, the Ti/TiO$_2$ NTA electrode provided a large number of active sites thereby enhancing the adsorption capacity of organic pollutant molecules.

3.2. Composition analysis

The XRD characterization was conducted to further study the Ti/TiO$_2$ electrode material. Figure 4 shows the XRD diffraction pattern of the Ti/TiO$_2$ NTA electrode. It only shows the peaks of Ti and anatase TiO$_2$. The characteristic peaks of the anatase phase appear at 2θ of 26.35°, 37.78°, 48.08°, 53.92°, 55.11°, 62.73°, etc., corresponding to (101), (004), (200), (105), (211), (204), etc. crystal plane diffraction peaks of anatase phase (PDF card No. 21-1272 of the anatase phase TiO$_2$) (Daghrir et al. 2012, 2013). It indicates that the composition of the prepared nanotube array electrode is mainly anatase TiO$_2$. 

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3.3. Electrochemical performance

The electrochemical tests were performed for the LSV curves (Figure 5) to analyze the properties of the test electrodes (Ti sheet and Ti/TiO2 NTA electrodes) over the Pt electrode. As illustrated in Figure 5, the steady-state polarization curves of the Ti and the Ti/TiO2 NTA electrodes have no oxidation peaks in the scanning range from 0.0 to 3.0 V. The oxygen evolution potential (OEP) of the prepared Ti/TiO2 NTA electrode was approximately 2.48 V (vs. SEC), which was higher than that of the Ti one. It was ascribed to the higher surface area of the Ti/TiO2 NTA electrode as compared to the Ti one, providing more active sites and enhancing the conductivity (Chen et al. 2020b, 2021). Since the hydroxyl radicals (·OH) were reacted to O2 to consume a large amount of active oxygen (Equations (2) and (3)), the oxygen evolution reaction (OER) was the main competitive side reaction against the oxidative degradation of organic pollutants. Therefore, compared with the Ti electrode, the Ti/TiO2 NTA electrode with higher OEP can inhibit the occurrence of OER and increase the generation of ·OH (Equation (4)), thereby promoting the electrochemical oxidation efficiency of organic pollutants (Equation (5)) (Yu et al. 2014; Chen et al. 2020a; Xu et al. 2021). Thus, considering the OEP and oxidation overpotential, the prepared Ti/TiO2 electrode was...
a satisfying choice for this work.

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\begin{align*}
&M(-\text{OH}) + 1/2\text{O}_2 + \text{H}^+ + \text{e}^- + \text{M} & \quad (2) \\
&M(-\text{OH}) + \text{H}_2\text{O} \rightarrow \text{O}_2 + 3\text{H}^+ + 5\text{e}^- + \text{M} & \quad (3) \\
&M + \text{H}_2\text{O} \rightarrow M(-\text{OH}) + \text{H}^+ + \text{e}^- & \quad (4) \\
&M(-\text{OH}) + \text{R} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{M} & \quad (5)
\end{align*}
\]

Herein, M represents the electrode material and R is for the representative organic pollutants (Saha et al. 2020; Chen et al. 2021).

### 3.4. Electrocatalytic degradation and electrolysis kinetics

The Ti/TiO$_2$ NTA electrode was used for the electrochemical degradation of the representative organics with an initial COD value of 50 mg/L by chronoamperometry. Figure 6 illustrated the curves of the degradation rates over different electrochemical oxidation time, besides, the organic degradation on the Ti/TiO$_2$ NTA electrode at different temperatures were also in assessment. As the temperature increased from 298 to 328 K, the degradation effect of the organics (An, RhB, and KHP) increased within 180 min of electrolysis, reaching the maximum values of 97.6%, 96.8%, and 71.1% at 328 K, respectively. It was because that higher temperatures were more likely to cause the organic pollutants to diffuse toward the electrode. On the other hand, the degradation behavior of the different organic substances on the surface of the prepared electrode

![Figure 5](image1.png)  
**Figure 5** | LSV curves of the test electrodes in 0.1 mol/L Na$_2$SO$_4$ at a scan rate of 50 mV/s.

![Figure 6](image2.png)  
**Figure 6** | Degradation rates of aniline (a), rhodamine B (b), and potassium hydrogen phthalate (c) over electrochemical oxidation time at different temperatures.
was different. In the electrochemical process, the degradation mechanism of organic pollutants can be divided into direct oxidation and indirect oxidation. (Chen et al. 2021) Direct oxidation occurred through the direct transfer of electrons on the surface of the Ti/TiO2 NTA electrode (Equation (4)) and was affected by temperature due to the degree of diffusion. Indirect oxidation referred to the process that organic pollutants were oxidized by ·OH (Equation (5)). It was affected by the type of organic matter (Garcia-Segura et al. 2018; Shao et al. 2019; Chen et al. 2021).

In addition, the reaction of the organics on the surface of the Ti/TiO2 NTA electrode at different temperatures followed the quasi-first-order kinetic (Figure 7). Table 1 shows the related kinetic equations and parameters. The lnC of each representative organic decreased in proportion to the reaction time at temperatures from 298 to 328 K, and the correlation coefficients of the linear relationship were all above 0.99. It indicated that under the electrocatalytic reaction of the Ti/TiO2 NTA electrode, the ·OH was stably produced. It was a free radical reaction process, which conformed to the assumption of the first-order kinetic process.

According to the reaction rate constant (k) in Table 1, the curves of lnk vs. the reciprocal of temperature (1/T) were plotted in Figure 9. Combined with the Arrhenius formula, the activation energy (Ea) of the electrocatalytic degradation of the representative organics (An, RhB, and KHP) were calculated to be 14.25 kJ/mol, 18.56 kJ/mol, and 35.32 kJ/mol, respectively. Activation energy represents the minimum energy required for the reaction of the reactant. The lower activation energies in this experiment compared with the activation energy of the general chemical reaction (60–250 kJ/mol) indicated that the electrochemical degradation was easier to carry out. Thus, the electrocatalytic degradation of KHP required the highest energy among the other target organics. It may be because some groups played a major role in the electrochemical degradation process, such as ·OH, hydroxyl group (-OH), amino group (-NH2), amine group (-N≡), etc. These groups can promote the decolorization of dyes and enhance the degradability of organic pollutants. On the other hand, the molecular structure of RhB and KHP has inhibitory carboxyl groups (-COOH), which inhibits the electrocatalytic degradation of -OH. In contrast, the inhibitory effect of KHP was the most obvious, and the catalytic degradation efficiency of An with

Figure 7 | The curves of the organic concentration C vs. the reaction time T for aniline (a), rhodamine B (b), and potassium hydrogen phthalate (c) at different temperatures.

Figure 8 | The linear curves of lnk vs. 1/T for aniline (a), rhodamine B (b), and potassium hydrogen phthalate (c).
Table 1 | Kinetic equations and correlation coefficients of the representative organics at different temperatures

| Organics                          | Temperature (°C) | Linear regression equation | Kinetic constant k (min⁻¹) | R²   |
|-----------------------------------|------------------|-----------------------------|---------------------------|------|
| Aniline                           | 25               | ln(C) = -0.0121t + 0.5906   | 0.0121                    | 0.996|
|                                   | 35               | ln(C) = -0.0143t + 0.6784   | 0.0143                    | 0.994|
|                                   | 45               | ln(C) = -0.0179t + 0.7542   | 0.0179                    | 0.992|
|                                   | 55               | ln(C) = -0.0203t + 0.7818   | 0.0203                    | 0.994|
| Rhodamine B                       | 25               | ln(C) = -0.0094t - 2.2862   | 0.0094                    | 0.992|
|                                   | 35               | ln(C) = -0.0119t - 2.3732   | 0.0119                    | 0.990|
|                                   | 45               | ln(C) = -0.0163t - 2.3869   | 0.0163                    | 0.990|
|                                   | 55               | ln(C) = -0.0185t - 2.4281   | 0.0185                    | 0.991|
| Potassium hydrogen phthalate      | 25               | ln(C) = -0.0017t - 1.8617   | 0.0017                    | 0.992|
|                                   | 35               | ln(C) = -0.0027t - 1.8794   | 0.0027                    | 0.998|
|                                   | 45               | ln(C) = -0.0045t - 1.9003   | 0.0450                    | 0.993|
|                                   | 55               | ln(C) = -0.0063t - 1.8684   | 0.0063                    | 0.998|

Figure 9 | The linear curves of the net current (ΔI) vs. the COD concentration of the representative organic pollutants at the voltages of 2.0 V(a), 2.5 V(b), 3.0 V(c), and 3.5 V(d), measured by the Ti/TiO₂ NTA electrode. An, RbB, and KHP stand for aniline, rhodamine B, and potassium hydrogen phthalate, respectively.
the promoting group amino (-NH₂) was the highest. Therefore, the degradation reaction of An was the easiest to proceed with within this work.

These indicated that the Ti/TiO₂ NTA electrode possessed a high catalytic degradation ability for the representative organics. The nanotube structure of the electrode provided a larger amount of adsorption and attachment points for the organic molecules in the solution, thereby improving the electrocatalytic degradation efficiency of the electrode. It was also attributed to the increased catalytic activity of the TiO₂ catalyst as the temperature increased.

In summary, in the electrolytic degradation and electrolysis kinetics using the Ti/TiO₂ NTA electrode method, the degradation rate of the organics (An, RhB, and KHP) increased with the temperature increased from 298 to 328 K in 180 min of electrolysis. Besides, it was revealed in Figure 7 that the lnC of each representative organic decreased in proportion to the time at test temperature from 298 to 328 K, and the correlation coefficients of the linear relationship were all above 0.99. Furthermore, the activation energies of the organic matter (An, RhB, and KHP) were calculated to be 14.25 kJ/mol, 18.56 kJ/mol, and 35.32 kJ/mol, respectively in the electrocatalytic degradation. Therefore, the electrochemical reactivity relationship of the target organics was An > RhB > KHP.

### 3.5. COD determination by Ti/TiO₂ NTA electrode method

#### 3.5.1. COD determination of single-component solution

The net current over the COD concentration under different voltages was studied to investigate the linkage mechanism between electricity generation and the degradation of the organics.

As observed in Figure 9, in the range of 5–150 mg/L COD concentration, the current increased linearly with the increase of COD concentration for the single-component solution of the target organics. The related linear regression equations were shown in Table 2. In terms of the electricity generation mechanism, the used Ti/TiO₂ NTA electrode oxidized organic matter to produce electrons through electrochemical reaction (Equations (4) and (5)), thereby causing the current change (Zheng et al. 2008). Hence, higher COD concentration means that more organic matter can be degraded to generate more electrons, forming a higher current value. Xu et al. reported a similar view (Xu et al. 2021). Moreover, the net electrocatalytic current relationship of the organics was An > RhB > KHP under the same voltage. It indicated that the electrochemical reactivity relationship of the organics was An > RhB > KHP. Therefore, for a single-component solution, the net current (ΔI) not only increased in proportion to the COD concentration of each organic matter but also depended on the type of the organic matter. On the other hand, the increase of the voltage significantly affected the enhancement of electrocatalytic degradation. It was attributed to the increase of the direct oxidation, producing more -OH, which improved the efficiency of indirect oxidation and increased ΔI (Saha et al. 2020; Chen et al. 2021).

#### 3.5.2. COD determination of multi-component solution

To further determine the relationship between COD concentration and oxidation current, the multi-component mixed organic solutions with known COD concentration were analyzed and measured by the electrochemical method. In this work, the representative organics were chosen, depending on their different functional groups, such as An with promoting groups (-NH₂), RhB, and KHP with inhibiting groups (-COOH), as shown in Figure 1. Moreover, these organics all have benzene rings in structure, which makes it easy to compare their electrochemical reactions.

#### Table 2 | Linear regression equations of the net current (ΔI) and the COD concentration for the organic solutions of aniline, rhodamine B, and potassium hydrogen phthalate

| Voltage (V⋅vs. SEC) | Aniline | Rhodamine B | Potassium hydrogen phthalate |
|--------------------|---------|-------------|-------------------------------|
|                    | ΔI = 0.59·COD + 14.31 | ΔI = 0.53·COD + 11.50 | ΔI = 0.49·COD + 7.90 |
| 2                  | 0.991   | 0.996       | 0.996                         |
| 2.5                | 0.993   | 0.997       | 0.995                         |
| 3                  | 0.992   | 0.985       | 0.995                         |
| 3.5                | 0.998   | 0.999       | 0.982                         |

Linear regression equation: ΔI = μA⋅COD + mg/L
For the two-component organic solutions, the linear curves of $\Delta I$ vs. COD and the related linear regression equations were shown in Figure 10 and Tables 3 and 4. As observed in Figure 10(a)–10(d) for the mixed solution of An/KHP, the current increased linearly with the increase of COD concentration with the range of 10–110 mg/L. Furthermore, in Figure 10(d) and 10(e) for the mixed solution of An/RhB and RhB/KHP, the linear relationship between the $\Delta I$ and the COD value.
was also verified in the range of 5–50 mg/L COD concentration. The related linear equations with about 0.99 correlation coefficients were different for the mixed solutions in different proportions. The increased voltage enhanced the electrocatalytic process significantly. Moreover, the results showed that the net current was not only affected by the types of the organic pollutants but also depended on the volume ratios of the mixed solutions at the same COD concentration. It was because RhB and KHP possessed -COOH groups that inhibited the electrocatalytic degradation of -OH. However, An has the promoting -NH2 groups. According to Equation (4), the promoting groups promoted the consumption of -OH due to the oxidation of organic matter, while the inhibitory groups were the opposite. Therefore, the specific characteristics of the target organic matter affected the process of generating electrons, thereby affecting the current (Yu et al. 2014; Chen et al. 2020a; Vaiano et al. 2020; Xu et al. 2021).

As shown in Figure 11 and Table 5, the net current of the three-component mixed solutions with known COD concentration in the range of 10–110 mg/L was determined by the prepared Ti/TiO2 NTA electrode. Under a voltage of 2.5 V (vs. SCE), there were good linear relationships between ΔI and COD for the three-component solutions with different ratios, and the correlation coefficients were all about 0.99. Besides, the catalytic current was affected by the different volume ratios of the organic solutions. The net current of the An/RhB/KHP solution with a 4:5:1 volume ratio was the largest at the same COD value, while the one with a 1:2:7 volume ratio was the smallest. It was due to the difference in electrochemical reactivity

### Table 3 | Linear regression equations of net current ΔI and COD value of the two-component solutions of An/KHP

| An:KHP | Voltage (V vs. SEC) | Linear regression equation (ΔI, μA; COD, mg/L) | R² | 2:8 | Linear regression equation (ΔI, μA; COD, mg/L) | R² | 3:7 | Linear regression equation (ΔI, μA; COD, mg/L) | R² |
|--------|---------------------|-----------------------------------------------|-----|------|-----------------------------------------------|-----|------|-----------------------------------------------|-----|
| 1:9    | 2                   | ΔI = 0.49·COD + 9.36                           | 0.997| ΔI = 0.52·COD + 9.71                           | 0.997| ΔI = 0.54·COD + 9.90                           | 0.996|
|        | 2.5                 | ΔI = 1.82·COD + 134.49                         | 0.997| ΔI = 1.94·COD + 143.09                         | 0.998| ΔI = 1.98·COD + 153.38                         | 0.998|
|        | 3                   | ΔI = 11.09·COD + 420.87                        | 0.994| ΔI = 11.58·COD + 446.66                        | 0.996| ΔI = 11.93·COD + 492.89                        | 0.997|
|        | 3.5                 | ΔI = 12.18·COD + 770.28                        | 0.988| ΔI = 12.41·COD + 852.68                        | 0.994| ΔI = 12.73·COD + 933.34                        | 0.997|
| 2:8    | 4                   | ΔI = 0.56·COD + 10.27                          | 0.993|                                               |      |                                               |      |
|        | 2.5                 | ΔI = 2.27·COD + 155.96                         | 0.989|                                               |      |                                               |      |
|        | 3                   | ΔI = 12.33·COD + 511.98                        | 0.995|                                               |      |                                               |      |
|        | 3.5                 | ΔI = 13.11·COD + 981.85                        | 0.999|                                               |      |                                               |      |
| 3:7    | 4.6                 | ΔI = 0.58·COD + 10.92                          | 0.993| ΔI = 1.98·COD + 155.34                        | 0.995|                                               |      |
|        | 2.5                 | ΔI = 2.45·COD + 167.29                         | 0.981| ΔI = 12.83·COD + 543.83                       | 0.991|                                               |      |
|        | 3                   | ΔI = 12.83·COD + 543.83                        | 0.991|                                               |      |                                               |      |
|        | 3.5                 | ΔI = 12.88·COD + 1,112.49                     | 0.997|                                               |      |                                               |      |

An and KHP stand for aniline and potassium hydrogen phthalate, respectively.

### Table 4 | Linear regression equations of net current ΔI and COD value of the two-component solutions of An/RhB and RhB/KHP

| Volume ratios | An:RhB | RhB:KHP | Linear regression equation (ΔI, μA; COD, mg/L) | R² | Linear regression equation (ΔI, μA; COD, mg/L) | R² |
|---------------|--------|---------|-----------------------------------------------|-----|-----------------------------------------------|-----|
| 1:9           | ΔI = 1.78·COD + 180.33 | 0.991 | ΔI = 1.69·COD + 142.13                         | 0.993|
| 2:8           | ΔI = 1.98·COD + 184.10 | 0.994 | ΔI = 1.74·COD + 148.27                         | 0.992|
| 3:7           | ΔI = 2.30·COD + 188.58 | 0.990 | ΔI = 1.68·COD + 155.34                        | 0.995|
| 4:6           | ΔI = 2.43·COD + 193.36 | 0.995 | ΔI = 1.65·COD + 161.87                        | 0.990|
| 5:5           | ΔI = 2.46·COD + 196.68 | 0.995 | ΔI = 1.72·COD + 168.05                        | 0.995|

An, RhB, and KHP represent aniline, rhodamine B, and potassium hydrogen phthalate, respectively.
(An > RhB > KHP) and the functional groups of the target organics. Therefore, the linear relationship between $\Delta I$ and COD was different for the detection of multi-component mixed solutions of different proportions.

Table 6 summarizes the salient properties of recently developed electrodes for COD detection. The electrode preparation method, linear equation, target organic solution, operation time, etc. in the comparison table show that our research has conducted a more comprehensive and complete study on COD determination using the prepared Ti/TiO$_2$ electrode, especially for the detection of single-component and multi-component solutions. Although Zhang et al. and Diksy et al. mentioned multi-component solutions in their work, they did not conduct in-depth research and discussion on different types and ratios of organic solutions (Zhang et al. 2009; Diksy et al. 2020). However, this part of the research is of great significance for an actual measurement. In this work, a secondary anodic oxidation method was used to convert Ti electrodes into Ti/TiO$_2$ nanotube array electrodes with a high-efficiency contact area and multiple active sites. The preparation method is simple and easy to achieve in a short time, without any complex procedures and expensive instruments, compared to the detection method of photoelectrocatalysis (Li et al. 2006a, 2006b, 2007; Zhang et al. 2009), the instruments for preparation (Li et al. 2006a, 2006b, 2007; Zhang et al. 2009; Ma et al. 2011; Mo et al. 2015; Kabir et al. 2019; Diksy et al. 2020), and the preparation time (Li et al. 2006a, 2006b, 2007; Zhang et al. 2009; Ma et al. 2011; Mo et al. 2015; Abdel-Salam et al. 2018; Carchi et al. 2019; Diksy et al. 2020). The effect of the types and ratios of the organics on COD measurement by the Ti/TiO$_2$ electrode method was studied and discussed in the range of 5–150 mg/L COD. It was revealed that organic compounds with different functional groups influenced electrochemical COD determination. For future research, it is of great significance to improve the work of electrochemical method for COD determination by developing new electrode preparation methods and studying the influence of different types and proportions of organic pollution on the COD measurement results.

In summary, the net current $\Delta I$ had a good linear relationship with the COD value of the measurement range for single-, two-, and three-component solutions using the prepared Ti/TiO$_2$ NTA electrode method, and the correlation coefficients were all about 0.99. In addition, the different linear relationship of each mixed organic solution was due to the electrochemical reactivity. Therefore, under the same COD concentration, the oxidation current of each mixed organic solution was different.
It illustrated the difference in the electrocatalytic kinetic behavior of organic substances on the prepared Ti/TiO₂ electrode. Therefore for an early stage of technological applications for Ti/TiO₂ NTA (Zheng et al. 2008; Dai et al. 2020), advanced fitting methods and preparation methods need to be improved and developed.

4. CONCLUSIONS

In summary, we have demonstrated a COD measurement method based on a prepared Ti/TiO₂ NAT electrode. The Ti/TiO₂ electrode with nanotube array (NTA) structure was prepared by the secondary anodic oxidation method. The composition of the electrode was mainly anatase phase TiO₂, the average inner diameter of the nanotube was ∼100 nm, and the wall thickness was ∼20 nm. The prepared Ti/TiO₂ NTA electrode was used for electrocatalytic degradation of different organic substances (including An, RhB, and KHP). Thus, the macro-kinetics of the electrocatalytic oxidation of organic compounds on the electrode surface were studied and discussed, conformed to the first-order kinetic reaction. Compared with the electrode reaction activation energy of the organics, the difference in the dynamic behavior of the organic substances on the electrode surface was revealed. Furthermore, using An, RhB, and KHP as target pollutants, the Ti/TiO₂ NTA electrode electrochemical method was used to determine the COD concentration of single-component, two-component, and three-component mixed organic solutions. It was found that the COD value of the solution was directly proportional to the anodizing current, and the correlation coefficients were all about 0.99. It confirmed the feasibility of COD determination of organic solutions using the prepared Ti/TiO₂ electrode. In addition, the oxidation current of the organic substances was different

| Electrode | Preparation method | Detection method | Linearity range (mg/L) | Target substance | Operation time (s) | reference |
|-----------|--------------------|------------------|------------------------|-----------------|-------------------|-----------|
| Ti/TiO₂ photoelectrode | Laser Anneal | Photoelectrocatalysis | 50–2,000 | S: KHP | > 30 | Li et al. (2006b) |
| Ti/TiO₂/PbO₂ photoelectrode | Dip-coating combined with laser anneal | Photoelectrocatalysis | 20–2,500 | S: KHP | > 30 | Li et al. (2007) |
| Carbon fiber felt/β-PbO₂ electrode | Electrochemical deposition | Electrochemical catalysis | 50–5,000 | S: NaAc, LA, NaCO, Glu, Xyl, HQ, Cys, GmA, p-HbA, p-Np, and KHP | > 120 | Mo et al. (2015) |
| Pseudo-graphite electrode | Chemical vapor deposition method | Electrochemical catalysis | 0–1 × 10⁴ | S: Glu, KHP, SDBS, and LA | – | Kabir et al. (2019) |
| Nano-Cu/C electrode | Electrochemical deposition | Electrochemical catalysis | 32–256 | M: Gly and Glu (ratio of 1:1) | > 120 | Diksy et al. (2020) |
| Ti/Sb-SnO₂/PbO₂ composite electrode | Electrochemical deposition | Electrochemical catalysis | 0.5–200 | S: Glu, Su, Np, HQ, p-HbA, and Te | > 30 | Ma et al. (2011) |
| Mixed-phase TiO₂ electrode | Dip-coating | Photoelectrocatalysis | 0–200 | S and M: KHP, Glu, GrA, SuA, MaA, and Glu-GtA | – | Zhang et al. (2009) |
| Ti/TiO₂ electrode | Anodic oxidation | Electrochemical catalysis | 20–2,500 | S: KHP | 100 | Ge et al. (2016) |
| Ti/TiO₂ nanotube array electrode | Secondary anodic oxidation | Electrochemical catalysis | 5–150 | S and M: An, RhB, and KHP | 60 | This work |

S and M stand for single- and multi-component organic solutions, respectively. An, RhB, and KHP represent aniline, rhodamine B, and potassium hydrogen phthalate, respectively. The similar representative names include: Cys – cysteine, Glu – glucose, Gly – glycine, GmA – glutamic acid, GrA – glutaric acid, HQ – hydroquinone, LA – lactic acid, MaA – malonic acid, NaAc – sodium acetate, Na₂C₂O₄ – sodium oxalate, Np – nitrophenol, p-HbA – p-hydroxybenzoic acid, p-Np – p-nitrophenol, Su – sucrose, SuA – succinic acid, SDBS – sodium dodecyl benzenesulfonate, Te – tetracycline, Xyl – xylose.
under the same COD concentration, reproving the electrocatalytic kinetic behavior of the organic substances on the electrode surface. Therefore, the oxidation current was related to the COD concentration and the types of organic matter. Furthermore, due to the attractive usability and reusability properties with advantages of simple preparation method, fast detection, expenses reduction, and energy saving for the Ti/TiO2 NTA electrode, this report offered a feasibility study for COD determination, electrochemical degradation of water pollution, and other electrochemical processes based on Ti/TiO2 electrodes, especially for detection and monitoring of actual wastewater samples containing organic pollutants.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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