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Short Communication

Electrochemical Determination of Chemical Oxygen Demand Using Ti/TiO_2 Electrode

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To overcome the shortcomings of the conventional potassium dichromate method (PDM) for monitoring chemical oxygen demand (COD) of waters, many efforts have been made on developing quick and environment-friendly techniques. Among all alternatives, electrochemical (EC) techniques are very competitive due to their relatively simple devices and quickness. A number of electrodes have been fabricated to investigate electrochemical determination of COD. However, little work has been reported on TiO_2 based electrode for this purpose. In the present work, Ti/TiO_2 electrode was simply prepared by anodic oxidation of pure titanium. Aqueous solutions of potassium hydrogen phthalate and phenol were electrolyzed by chronocoulometry in a three-electrode system with Ti/TiO_2 as working electrode (anode). Organic compounds were electrochemically oxidized on Ti/TiO_2 electrode by hydroxyl radicals and the released electrons were recorded and transferred to currents. The electric currents were proportional to the COD values of the water samples being investigated. Based on data of COD values and corresponding currents, a linear regression equation was obtained for a certain kind of waste water. With the regression equation, current of an unknown water sample was transferred to its COD value. Conditions for the presented EC method were set up as cell voltage 2.0V *v.s.* SCE and pH 7.0. The linear range of COD was of about 25~530 mg/L. COD values of real waste water samples were measured by Ti/TiO_2 electrode and the relative errors were all in the range of ±8% compared with data determined by conventional PDM. The electrochemicalmethodology was successfully applied to evaluate COD in waste water..

Keywords: Ti/TiO_2 electrode; anodic oxidation; chemical oxygen demand; chronocoulometry

1. INTRODUCTION

Chemical oxygen demand (COD) is widely used as a parameter to evaluate the amount of organic pollutants in wastewater, the most important index in monitoring water quality, managing effluent quality, and controlling the degree of pollution in water. COD is defined as the demand of oxygen required for the oxidative degradation of organic compounds by strong oxidizing agents, such as dichromate and permanganate). The conventional process of COD measurement, known as potassium dichromate method (PDM, National Standard of China, GB 11914-1989), consists of catalytic oxidization, reflux and titration. In that process, known amount of excessive oxidant ($K_2Cr_2O_7$), certain amount of catalyst ($AgNO_3$ in H_2SO_4 solution), chlorine ion masking agent ($HgSO_4$) are added into the contaminated water sample, followed by refluxing at 140℃ for 120min. After the digested sample is cooled to room temperature, the excess oxidant is titrated by Fe^{2+}. Shortcomings of the conventional method include long time consumption (3~4h), use of expensive ($AgNO_3$), toxic ($K_2Cr_2O_7$, $HgSO_4$) and strongly corrosive (H_2SO_4) chemicals, disturbance of chlorine ion, and dependence of measurement accuracy on operating proficiency [1, 2]. Limited by these drawbacks, potassium dichromate method is quite difficult to apply for on-site evaluation or on-line monitoring of pollution levels of wastewater.

To overcome the disadvantages of conventional PDM, numerous efforts have been made in developing rapid and environmentally friendly new methods for COD measurement. To date, alternatives to conventional PMD could largely be divided into three categories. The first category involves refinements of PMD, such as reduction in consumption of time and chemical reagents, spectrophotometry instead of titration [3]. Based on conventional PMD, Jirka et al [3] carried out the digestion step in sealed glass tubes rather than digesting by reflux, and Cr^{3+}, instead of Cr(VI), was spectrophotometrically measured. The key benefits of the so-called micro semi-automated method were that the wastewater samples were digested in a batch, in which the chemical consumption was reduced by a factor of 20, and precision was greatly improved. Since its establishment, this method as a whole, or its digestion approach, has been widely used [4-6]. Guesta et al [1] used a microwave oven for sample digestion in conjunction with a flow injection system in which Cr^{3+}) and Cr(VI) were separated in an anion exchange resin, subsequently, Cr(VI) was detected by flame atomic absorption spectrometry. More recently, Guesta et al [7] replaced the anion exchange step by liquid extraction of Cr(VI) with tributyl phosphate to obtain approximately the same detection concentration range and limit. Dan et al [8] shortened the digestion time to 15 min by using the mixed acid, $V(H_3PO_4):V(H_2SO_4)=1:10$), and determined the access Cr(VI) by single sweep polarography. Hu et al [2] detected the concentration of Cr^{3+} after digestion with a photodiode luminometer based on the chemiluminescent reaction of luminol-H_2O_2-Cr^{3+} system. In all of these kinds of methods, main toxic chemicals used in conventional PDM are still used, and therefore cannot avoid secondary pollution.

The second category involves direct or indirect determination of COD by spectroscopic analysis, including Ultraviolet–visible (UV–vis) spectroscopy [9], fluorescence spectroscopy [10,11] and near-infrared spectroscopy [12,13]. UV-vis spectroscopy has been applied more extensively. Matsche et al [9] reported good correlations between UV absorbance values at 260 nm wavelength and COD concentrations in sewage. More recently, the combination of UV with partial-least squares regression has shown to estimate TSS (total suspended solids) or COD concentrations [12, 14, 15]. Spectroscopic techniques for COD monitoring presents several advantages such as: fast response and no further addition of chemicals. Nevertheless, it is difficult to eliminate the negative impacts on the estimation accuracy of spectroscopic analysis due to turbidity and internal interactions of contaminants in water samples.

Methods of the third category are based on catalytic oxidation reactions on electrodes, including electrochemical (EC) techniques [16-26], photoelectrochemical (PEC) techniques [27-32], and photocatalytic (PC) oxidation techniques [33-35]. Kim et al [34, 35] used TiO_2 powder as a photocatalyst to oxidize organic substances by ultraviolet (UV) light, and also a sensor of dissolved oxygen was employed. They proposed that the decrease of dissolved oxygen concentration in water sample was proportional to the COD values. The main drawbacks of photocatalysis were the low photocatalytic efficiency and the poor reproducibility resulted from oxygen content in water sample [27]. In the PEC methods, organic substances in water sample are oxidized by special electrodes under UV lights, and the generated electrical signals, which are in proportion to COD concentrations, are measured [31]. The most commonly used sensing electrodes are comprised of TiO_2, such as $Ti/TiO_2/PbO_2$ [36], glass/indium tin oxide (ITO)/TiO_2 [27], Ti/TiO_2 nanotubes [28], ITO/TiO_2 [29], $Ti/TiO_2/Cu_2O$ [30], Ti/TiO_2/Pt NPs [31], and Ti/TiO_2 [32]. Though, compared with PC methods, the oxidation capacity and efficiency of PEC are improved, the use of UV light raises complexity and cost of the monitoring equipment [21, 28]. Over the last decades, EC techniques have been developed for COD measurement, in which organic substances were oxidized on surface of a working electrode. An electrical current was generated from the electrochemical oxidation and it was related to the COD value of the water sample [17]. EC methods for measuring COD have been considered as promising techniques due to their numerous advantages, such as rapidness, sensitiveness and easy manipulation [22]. In an EC process, hydroxyl radicals ($\cdot OH$) are produced on the working electrode surface and act as an oxidant which is capable of oxidizing organic substances and forming water and carbon dioxide as products [17, 18, 21, 24, 26]. Several types of electrodes have been reported, such as Cu [16, 20], CoO [22], Pt/PbO_2 [17], glass carbon/NiCu [23], Ti/Sb-SnO/PbO_2 [21], and boron-doped diamond (BDD) [18, 19, 24-26].

Processes for fabrication of TiO_2 based electrodes for PEC methods were quite complicated and therefore costly [27-32]. And little work has been reported about TiO_2 based electrodes used in EC methods for COD measurement. To the best of our knowledge this is the first report to outline the electrochemical detection of COD using a chronocoulometric technique combined with an in-house Ti/TiO_2 electrode prepared by anodic oxidation of pure titanium. Furthermore, the electrochemical methodology was successfully applied towards the detection of COD in waste water.

2. EXPERIMENTAL

2.1 Materials

Potassium hydrogen phthalate ($C_8H_5O_4K$, KHP) was of guarantee grade, all other chemicals, phosphoric acid, sodium hydroxide, potassium dichromate, sulphuric acid, silver nitrate, mercury sulfate and ammonium ferrous sulfate, were of analytical grade and used without further treated. Only redistilled water was used in this work.

Solutions of KHP and phenol were used as standard COD samples. 1.700g of KHP was dissolved in 100ml of water and then diluted with water to 1000.0m to get the stock solution with COD value of 2000.0 mg/L. COD value of stock solution of phenol was determined by PDM. Real waste water samples were collected from the influent and effluent of the sewage plant located in South of Shenyang, China.

Series of standard solutions with gradient known COD values were prepared from KHP and phenol stock solutions, respectively. The pHs were adjusted by adding 0.050M H_3PO_4 and 0.10M NaOH.

2.2 Fabrication of Ti/TiO$_2$ electrode

Pure titanium flake (purity > 99.9%) with dimensions of 8mm×8mm×1.5mm was used as substrate. The flake was polished by 1200# metallographic abrasive paper. Then it was subsequently washed with water, acetone, mixed acid of HF and HNO_3 (volume ratio 1:3) and water, sequentially. In the anodizing cell, the cleaned Ti flake was employed as the anode, and graphite was used as the cathode. Anodic oxidation of Ti flake was carried out in 1M NaOH solution under 20V DC at 55^{o}C for 30min. The obtained Ti/TiO_2 electrode was rinsed with water several times and preserved in water for further use. The Ti/TiO_2 electrode was characterized by X-ray diffraction (XRD) using a X’pert Pro diffractometer (PANalytical, Holland) with Cu Kα radiation.

2.3 Electrochemical measurement

COD tests were performed on an electrochemical working station (CHI660B, Shanghai Chenhua Instrument Co. Ltd., China). The test cell was consisted of a three-electrode system, prepared Ti/TiO_2 was employed as the working electrode (anode), platinum slice as counter electrode (cathode), and a saturated calomel electrode (SCE) as reference electrode. Based on chronocoulometry, 50ml standard COD solutions were electrolyzed for 30s. Chronocoulometric curves were recorded and used to determine the electric current, which was proportional to the COD value of the solutions [17]. A chronocoulometric curve was the plot of electric charge *v.s.* time, whose slope was the current, I_{COD}. Measurement of each COD sample was run for six times.

2.4 COD measurement of real samples by PDM

The COD values of real samples were measured by conventional PDM. 20 mL of real waste water, 20 ml of 0.050M $K_2Cr_2O_7$ solution, 30 ml of $AgNO_3/HSO_4$ solution (5 g $AgNO_3$ in 500 ml H_2SO_4), and 0.1 g $HgSO_4$ were put into a flask. The mixture was refluxed at 165 °C for 2 h. When cooled to room temperature, the excess potassium dichromate was determined by titration using 0.10M $(NH_4)_2Fe(SO_4)_2$ as the titrant. COD value of the sample was calculated according to National Standard of China GB 11914-89.

3. RESULTS AND DISCUSSION

3.1 Characterization of Ti/TiO$_2$

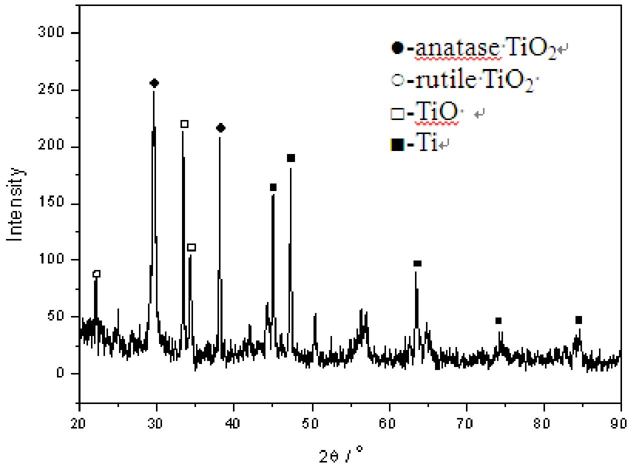
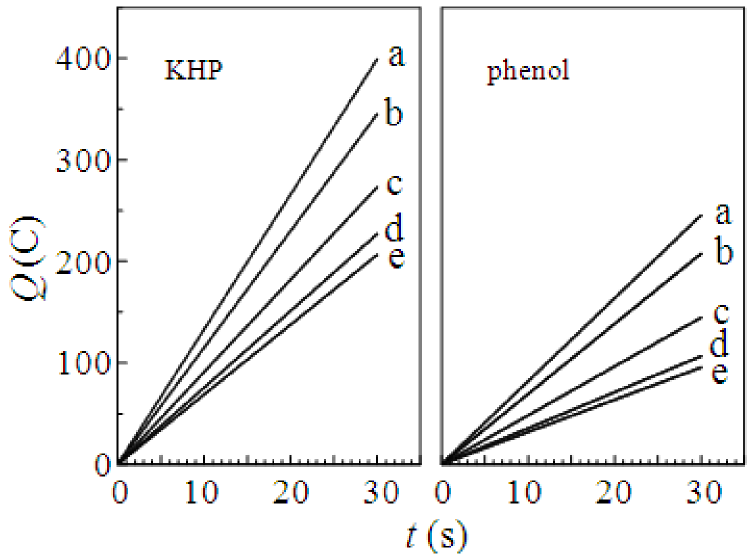


Figure 1. XRD patterns of Ti/TiO$_2$ electrode

The X-ray diffraction pattern of Ti/TiO$_2$ electrode surface was measured on a X'pert Pro diffractometer (PANalytical, Holland), as shown in Fig. 1. The surface of Ti/TiO$_2$ was a mixture of different types of titanium oxides, including anatase TiO$_2$, rutile TiO$_2$, and TiO [37]. The occurrence of metal Ti meant that the anodic film was thin.

3.2 Cell voltage

When a certain voltage was applied to the Ti/TiO$_2$ electrode, water molecules adsorbed on TiO$_2$ surface would be decomposed into hydroxyl radicals (·OH) [21, 38-40]. ·OH radical is a strong oxidant that can oxidize organic compounds into carbon dioxide and water [26], and the released electrons during electrochemical oxidation can be measured as an electrical current. Fig. 2 shows the chronocoulometric curves of KHP and phenol solutions, both with COD values of 200 mg/L, at pH 7.0. In the range of cell voltage 1.2V ~ 2.0V *v.s.* SCE, all chronocoulometric curves were linear, whose slopes were the electrolytic currents, I_{COD}. The higher the voltage applied, the greater the current measured. Fig. 3 shows the relationship between cell voltage and current for solutions of KHP and phenol with COD values of 200mg/L at pH 7. When the cell voltage was less than 1.0V *v.s.* SCE, the current was too low to guarantee measuring accuracy. When cell voltage was larger than 2.0V *v.s.* SCE, the measured chronocoulometric curves were nonlinear. Therefore, in the following studies, all experiments were carried out with the cell voltage set up as 2.0V *v.s.* SCE. Under the same cell voltage, current of KHP solution was larger than that of phenol solution, meaning that electrochemical reactivity of KHP was higher than that of phenol.



a-2.0 V; b-1.8 V; c-1.5 V; d-1.3 V; e-1.2 V (*v.s.* SCE)

Figure 2. Chronocoulometric curves of KHP and phenol solutions (COD 200 mg/L, pH 7.0)

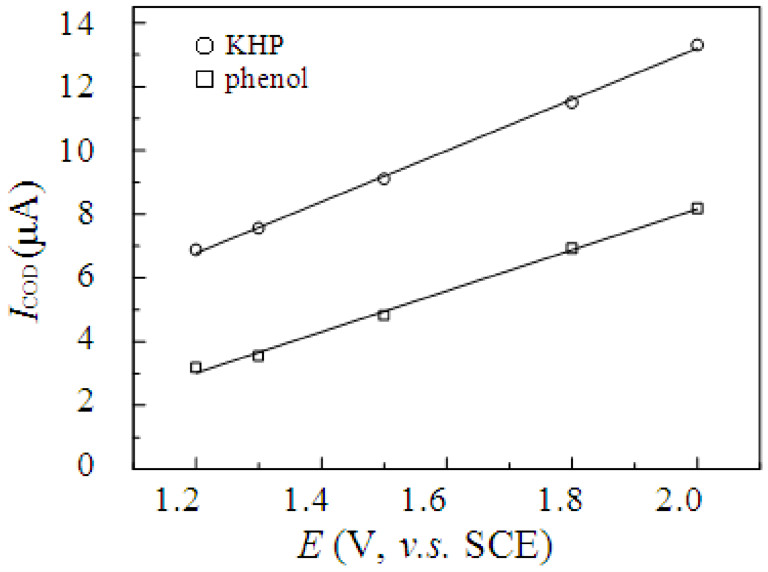


Figure 3. Relationship between cell voltage E and current I_{COD} (COD 200mg/L, pH 7.0)

3.3 pH

Fig. 4 shows the effect of pH on electric currents using a cell voltage of 2.0V *v.s.* SCE and COD of 200mg/L. In tested pH range of 4 to 10, electric current of both KHP and phenol solutions increased gradually with pH. It was believed that water was more readily oxidized to hydroxyl radicals in more alkaline media [18]. In alkaline solutions, the electrochemical evolution of oxygen occurred more and more easily with increasing pH [18, 23]. In the following studies, pH was set up as 7.0.

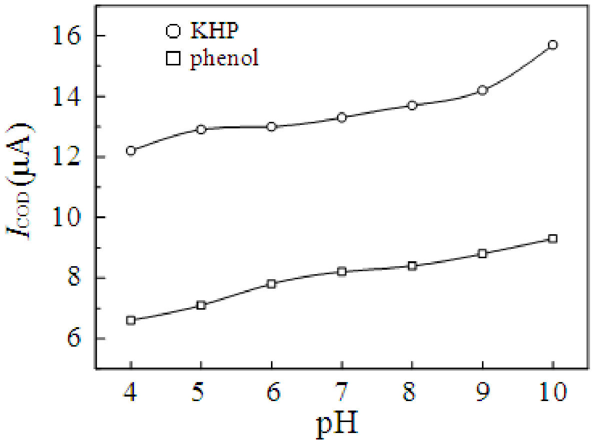


Figure 4. Influence of pH on current I_{COD} (Cell voltage 2.0V *v.s.* SCE, COD 200mg/L)

3.4 Relationship between current and COD

Fig. 5 shows the plots between COD values and currents for KHP and phenol, respectively, under cell voltage 2.00V *v.s.* SCE and pH 7. In accordance with cell voltage tests (Fig. 3) pH tests (Fig. 4), the current of KHP solution was higher than that of phenol at the same COD value. Linear regression equations of currents and COD values for KHP and phenol were calculated and given as Eq. 1 and Eq. 2, respectively.

$$I_{COD(KHP)} = 0.89 + 0.0635\ c \qquad (R^2 = 0.9983) \qquad (1)$$

$$I_{COD(phenol)} = 0.90 + 0.0363\ c \qquad (R^2 = 0.9959) \qquad (2)$$

Where I_{COD} is the current (μA), c is the COD value (mg/L), and R^2 is the regression coefficient.

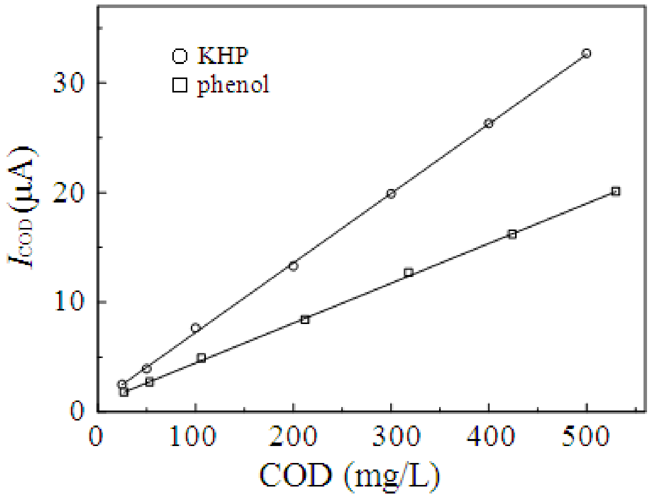


Figure 5. Relationship between COD values and current I_{COD} (Cell voltage 2.0V *v.s.* SCE, pH 7.0)

Electrochemical measurements of COD with other electrode, e.g., glass carbon/NiCu [23], Ti/Sb-SnO/PbO_2 [21], and (BDD [18], revealed that currents and COD values of all tested organic compounds fitted into the identical linear regression equation. Hence, when COD was determined electrochemically by the above mentioned electrodes was almost independent on the type of organic species [18, 21, 23]. In the present work, regression equations for KHP and phenol were different from each other. This is in agreement with what Yang et al reported on degradation kinetics of three sulfa pharmaceuticals [41] and three β-blockers [42] in TiO_2 aqueous suspension. They found that hydroxyl radical was responsible for the degradation, and that, under the same conditions, rate constants were different for each organic compound. Errami et al [43] and Melliti et al [44] reported that the rate constants of electrochemical oxidations happening on BDD electrode depended on the current density, concentration of the supporting electrolyte and temperature. Therefore, it is reasonable to suggest that the electrochemical reactivity of KHP was different from that of phenol on Ti/TiO_2 electrode.

As shown in Fig. 5, for both of KHP and phenol, regression coefficients were greater than 0.99, meaning that electrolytic currents and COD values had significant linear correlation. In the tested COD range of 25~530 mg/L, currents were in linear proportion to COD values, though the slope of KHP was greater than that of phenol.

3.5 Real samples

Principle of EC method for measuring COD values of water supposed in the present work is as follows. For a certain kind of waste water, its COD values are determined by standard PDM at first. Then these water samples with known COD values are electrolyzed by Ti/TiO_2 electrode, and their electric currents are recorded. Based on these data, a regression equation of the electric current and COD value of this kind of waste water established. The regression equation was used to transfer the current, which is determined by the presented EC method, to COD values of unknown waste water samples [18, 21, 23].

COD values of real samples were analyzed by both of the presented EC method and PDM, as listed in Table 1. The results showed that all relative standard deviations (RSD) of the presented EC method were less than 6.5%, and all relative errors between COD values determined by EC method and those determined by PDM were in the range of ±8%. The consistency between data obtained from EC method and PDM implied that Ti/TiO_2 electrode could be used to determine COD values of waste water [21, 23].

Table 1. COD values of real samples measured by EC method and PDM

Samples	COD[1] (mg/L)	RSD[3](n=6) (%)	COD[2] (mg/L)	Relative error (%)
Influent				
Sample 1	360.7	5.4	347.0	-3.8
Sample 2	439.4	5.5	420.9	-4.2
Sample 3	423.6	4.7	435.4	2.8
Effluent				
Sample 4	31.8	6.3	34.0	6.9
Sample 5	42.3	5.9	39.2	-7.3
Sample 6	33.3	6.3	34.8	4.5

1-Determined by EC method of the present work;
2-Determined by PDM;
3- Relative standard deviation.

4. CONCLUSION

Ti/TiO_2 electrode was prepared simply by anodic oxidation of substrate metal titanium, whose surface was composed of titanium oxides. Ti/TiO_2 electrode was used to measure COD values of water on an electrochemical working station by chronocoulometry. Solutions of KHP and phenol with known concentrations were used as standard water samples. Organic compounds were electrochemically oxidized on Ti/TiO_2 electrode by hydroxyl radicals and produced electric current, which was proportional to COD value of water sample. Currents depended upon species of organic compound, applied cell voltage and pH. When cell voltage and pH were fixed, currents were in linear proportion to COD values. The linear range of COD was about 25~530mg/L under cell voltage 2.0V *v.s.* SCE and pH 7.0. COD values of real waste water samples measured by Ti/TiO_2 electrode were in agreement with those measured by the conventional PDM. The method presented in this work was of quickness and accuracy in monitoring COD values of waters.

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