

Development of a Direct Photoelectrochemical Method for Determination of Chemical Oxygen Demand

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A novel rapid methodology for the determination of chemical oxygen demand (COD) based on photoelectrochemical oxidative degradation principle (PECOD) was proposed and experimentally validated. With this new method, the extent of degradation of dissolved organic matter in a water sample is measured simply by directly quantifying the extent of electron transfer at a TiO₂ nanoporous film electrode during an exhaustive photoelectrocatalytic degradation of organic matter in a thin layer photoelectrochemical cell. The PECOD method demonstrated in this work is a direct and absolute method. It does not require the use of standard for calibration. The method, in principle, measures the theoretical COD value due to the extraordinary high oxidation efficiency and accuracy of charge measurement. This new approach overcomes many of the current problems associated with existing oxygen demand techniques (e.g., the matrix effect, one of the serious practical problems that most rapid COD methods suffered because of the insufficient oxidation efficiency). The PECOD method overcomes the matrix effect by employing a highly effective photoelectrochemical system that is capable of fully oxidizing a wide spectrum of organics in the water sample. The method was successfully applied to determine the COD of a range of synthetic and real samples. Excellent agreement with a standard dichromate method was achieved. The practical detection limit of 0.2 mg L⁻¹ COD with the linear range of 0–200 mg L⁻¹ was also achieved. The PECOD method is a method that is environmentally friendly, robust, rapid, and easily automated. It requires only 1–5 min to complete an assay and consumes very limited reagent (electrolyte only).

The oxygen demand of water and wastewater represents one of the most important measurable parameters for water quality. At present, two standard analytical methodologies are in widespread use for the determination of the oxygen demand of waters and wastewaters. These are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Of the two, the COD method is preferred for assessing the oxygen demand of organic matters in heavily polluted water bodies. Consequently, COD has

been accepted as the national standard for organic pollution evaluation in many countries, such as Japan and China. The standard methods for determination of COD have been in place for many years.¹ These methods estimate the oxygen demand via oxidative degradation of the organic compounds present in the water samples. This oxidative degradation is carried out chemically via the use of strong oxidizing agents such as dichromate or permanganate. The extent of degradation is characterized by the amount of electrons transferred to the chemical oxidizing agent during chemical oxidation. This electron transfer is quantified indirectly by measuring, for example, dichromate depletion via titration or spectrophotometry. On the basis of the oxidizing agents used, the standard COD methods can be classified into either the dichromate method or the permanganate method. The former is more popular mainly due to its higher degradation degree toward a wide range of the organic pollutants.

Despite its widespread use, the standard dichromate method has several drawbacks. It requires a time-consuming (2–4 h) reflux process to allow for complete oxidation of the organic material. In addition, the method requires expensive (e.g., Ag₂SO₄), corrosive (e.g., concentrated H₂SO₄), and highly toxic (Hg(II) and Cr(VI)) reagents. The latter is of particular environmental concern and has led to the Cr(VI) method being abandoned in Japan. Because of these practical limitations, the dichromate standard COD method is difficult to be incorporated into an on-line, automated system and incapable of providing continuous real-time feedback, which is critical for applications such as large-scale environmental assessment and industrial process control where rapid and continuous feedback are needed.

In recent years, a great deal of effort has been devoted to the development of rapid and environmentally friendly new methods for the determination of COD.^{2–10} All these new developments

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have been based on either electrocatalytic^{2–5} or photocatalytic^{6–10} oxidation principles. Although the electrocatalytic oxidation method has demonstrated many advantages over the traditional COD methods such as the rapidity of the analysis, the directness in the acquisition of analytical signal, and the ease to be incorporated into on-line analysis monitoring system,^{2–5} the reliability of these new methods are still far from being the satisfied for practical use. This is mainly due to the fact that the electrocatalytic oxidation method is incapable of oxidizing a wide spectrum of organic compounds indiscriminately. The photocatalytic oxidation approach on the other hand, utilizes TiO₂ particles as photocatalyst to replace the traditional oxidizing agent (e.g., Cr(IV)). In this process, the oxygen concentration change during the photocatalytic degradation is measured as the analytical signal using a pair of oxygen electrodes. This depletion of O₂ is then correlated with standard COD methods.^{6–10} The photocatalytic degradation approach is more promising in comparison with electrocatalytic degradation methods due to the strong oxidation power of illuminated TiO₂ particles. Despite this, the approach has suffered from several problems. These include the low fraction of degradation, which is a tradeoff for a faster analysis time; low sensitivity caused by the small change in oxygen concentration during degradation; limited dynamic working range due mainly to the low solubility of oxygen in water; and the need to control experimental temperature since oxygen concentration measurement by oxygen electrode is highly temperature dependent. Furthermore, the low degradation efficiency makes the method matrix dependent, thus requiring the system calibration in order to correct for this influence. Because the COD is an aggregative parameter, it is difficult to define an appropriate calibration standard that would be universally applicable to all matrixes. This is not just an inconvenience for the system operation, but it would also impact the accuracy and reproducibility of the method. In summary, a significant improvement is required before this method can be practically used. This has agreed on by the authors themselves as they describe the method as “the responses were neither sensitive enough nor reproducible”.^{6,8}

The fundamentals of photoelectrochemistry and heterogeneous photocatalysis at semiconductors have been well-documented.^{11,12} Extensive studies of photocatalytic oxidation processes at TiO₂ surface for various applications have also been reported.^{13–17} In this study, we propose a unique approach in which the COD value of a sample is directly measured at a TiO₂ nanoparticulate semiconductor electrode via a photoelectrochemical oxidative degradation process, namely, the PECOD method.¹⁸ PECOD may also be referred to as photoelectrochemical COD. With this new

method, the extent of degradation of organic material is measured simply by directly quantifying the extent of electron transfer at a TiO₂ nanoparticle film electrode during an exhaustive photoelectrochemical catalytic oxidation process. The proposed quantitative relationship between the measured analytical signal and the COD values was experimentally validated. Importantly, this approach possesses the advantages of both the electrocatalytic approach and the photocatalytic approach while overcoming many of the problems associated with existing oxygen demand techniques.

EXPERIMENTAL SECTION

Materials and Sample Preparation. Indium tin oxide (ITO) conducting glass slides were commercially supplied by Delta Technologies Limited. Titanium butoxide (97%, Aldrich) and potassium hydrogen phthalate (AR, Aldrich) were used as received. Peptone, beef extract, glucose, and glutamic acid were purchased from Aldrich without further treatment prior to use. All other chemicals were of analytical grade and were purchased from Aldrich unless otherwise stated. High-purity deionized water (Millipore Corp., 18 M Ω ·cm) was used in the preparation of synthetic wastewater samples and in the dilution of real wastewater samples.

The OECD synthetic wastewater sample containing 150 mg/L peptone, 110 mg/L beef extract, and 30 mg/L urea was prepared according to the Organization for Economic Corporation and Development Guidelines (OECD) with a little modification.¹⁹ This synthetic sample is often used as a calibration standard for BOD and COD analysis systems.^{20,21} The GGA synthetic sample is often used for BOD₅ standard, which contains 150 mg/L glucose and 150 mg/L glutamic acid and was prepared according to the APHA standard methods.¹

The real samples used in this study were collected within the Queensland State in Australia from various industrial sites including wastewater treatment plants, sugar plants, brewery manufacturers, cannery manufacturers, and dairy production plants. All samples were preserved according to the guideline of the standard method. When necessary, both synthetic and real samples were diluted to a suitable concentration prior to the analysis. After dilution, the same sample was simultaneously analyzed by both standard COD method and PECOD method. The sample for PECOD method involved addition of NaNO₃ solid equivalent to 2 M as supporting electrolyte.

Preparation of TiO₂ Film Electrodes. Aqueous TiO₂ colloid was prepared by hydrolysis of titanium butoxide according to the method described by Nazeeruddin et al.²² The resultant colloidal solution contains 60 g dm⁻³ TiO₂ solid with particle size ranging from 8 to 10 nm. The ITO slide was used as the electrode substrate and was pretreated to ensure its cleanness. After pretreatment, the ITO slide was dip-coated in the TiO₂ colloidal solution. The coated electrodes were then calcined in a muffle furnace. The details of the electrode preparation was published in our previous

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work.^{23,24} The thickness of TiO₂ porous film was 1.0 μm measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

Apparatus and Methods. All photoelectrochemical experiments were performed at 23 °C in a thin layer three-electrode electrochemical cell with a quartz window for illumination. The thickness of the layer is 0.18 mm, the area of the layer is 0.75 cm², and the volume of the anodic compartment is 13.5 μL. A saturated Ag/AgCl electrode and a platinum mesh were used as the reference and the auxiliary electrodes, respectively. A voltammograph (CV-27, BAS) was used for application of potential bias in the photoelectrolysis experiments. Potential and current signals were recorded using a Macintosh computer (7220/200) coupled to a Maclab 400 interface (AD Instruments). Illumination was carried out using a 150-W xenon arc lamp light source with focusing lenses (HF-200w-95, Beijing Optical Instruments). To avoid the sample solution being heated up by the IR light, the light beam was passed through a UV band-pass filter (UG 5, Avotronics Pty. Limited) prior to illuminating the electrode surface. Standard COD value (dichromate method) of all the samples was measured with a COD analyzer (NOVA 30, Merck).

Correlation Analysis. The Pearson correlation coefficient was used as a measure of the intensity of association between the values obtained from the PECOD method and the standard COD method. This was employed for the data in Figures 4 and 5. To characterize the trend of the two-way scattergram in Figures 4 and 5, the slope of the principal axes of the correlation ellipse was calculated. This was done in preference to simple linear regression analysis since regression analysis assumes that the *x* values are measured with no (or negligible) error and that the *y* values are the dependent, normally distributed variables. This is not the case for correlation between PECOD values and the standard COD values.

RESULTS AND DISCUSSION

Analytical Signal Generation. Upon absorption of light by TiO₂, semiconductor electrons are promoted to the conduction band (*e*_{cb}⁻), and holes are left in the valence band (*h*_{vb}⁺). Spatially they are so close to each other as to be called electron/hole pairs, and they are easily recombined. At bulk semiconductor/electrolyte interface, the inner electric field separates the pairs spatially, prolonging the lifetime of the pairs. At TiO₂ nanoparticle surface for the case of TiO₂ nanoparticle photocatalytic slurry system, the electrons are trapped by the surface groups but still spatially very close to each other.^{16,25} As a result, in such system the efficiency of photons is more heavily dependent on the surface reaction kinetics for both the removal of electrons via reduction at the interface and the capture of holes via oxidation process. To photocatalytically degrade organic compounds in the water in the slurry system, an electron acceptor, such as oxygen, is required to remove the photoelectrons.¹⁶ The oxidation reaction of organic compounds by photoholes or surface trapped photoholes and the reduction reaction of electron acceptors take place on the same particle. The sluggishness of either process will cause the buildup of correspondent charge carrier facilitating the recombination of photoelectrons and photoholes.¹⁶

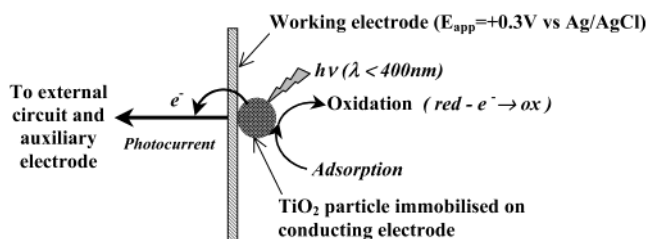
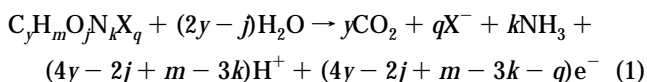


Figure 1. Schematic of the photoelectrocatalytic processes involved in the analytical signal generation.

The photohole is a very powerful oxidizing agent (+3.1 V) that will readily lead to the seizure of an electron from a species adsorbed to the solid semiconductor.¹⁶ Thermodynamically, both organic compounds and water can be oxidized by the photoholes or surface-trapped photoholes, but usually organic compounds are more favorably oxidized, which leads to the mineralization of a wide range of organic compounds.

In our approach, the TiO₂ nanoparticles were immobilized onto conducting substrate, forming nanoporous TiO₂ film electrodes. The electrodes possess a large surface area and the properties of the TiO₂ nanoparticle photocatalyst, which facilitates the photocatalytic oxidation of organic compounds over water oxidation. This TiO₂ nanoparticle film electrode is used as the working electrode in a thin layer three-electrode photoelectrochemical cell, and photoelectrons generated from the oxidation of organics are captured by electrochemical means. By applying an appropriate positive potential bias to the working electrode, the photocatalytic oxidation of organic compounds and water takes place at a working electrode. The photoelectrons are subsequently forced to pass into the external circuit and to the auxiliary electrode, where the reduction of water or oxygen takes place (see Figure 1). The photocurrent or charge is monitored and gives a direct measure of the oxidation of organic compounds, which can be used as the analytical signal.

Analytical Signal Quantification. Because of the strong oxidation power of photoholes, photocatalytic oxidation of organic compounds at TiO₂ electrode leads to stoichiometric oxidation (degradation) of organic compounds as follows:



where N and X represent a nitrogen and a halogen atom, respectively. The numbers of carbon, hydrogen, oxygen, nitrogen, and halogen atoms in the organic compound are represented by *y*, *m*, *j*, *k*, and *q*.

To minimize the degradation time and to maximize the degradation efficiency, the photoelectrochemical catalytic degradation of organic matter was carried out in a thin layer photoelectrochemical cell. This process is analogous to bulk electrolysis in which all of the analytes are electrolyzed, and Faraday's law can be used to quantify the concentration by measuring the charge passed if the charge/current produced is the result of photoelectrochemical degradation of organic matter. That is

$$Q = \int i dt = nFVC \quad (2)$$

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where n refers to the number of electrons transferred during the photoelectrocatalytic degradation, which equals $4y - 2j + m - 3k - q$ (see eq 1); i is the photocurrent from the oxidation of organic compounds; F is the Faraday constant; and V and C are the sample volume and the concentration of organic compound, respectively.

The measured charge (Q) is a direct measure of the total amount of electrons transferred that results from the complete degradation of all compounds in the sample. Since one oxygen molecule is equivalent to 4 electrons transferred, the measured Q value can be easily converted into an equivalent O_2 concentration (or oxygen demand). The equivalent COD value can therefore be represented as

$$\text{COD (mg/L } O_2) = \frac{Q}{4FV} \times 32\,000 \quad (3)$$

Equation 3 can be used to quantify the COD value of a sample since the charge (Q) can be obtained experimentally and for a given photoelectrochemical cell, the volume (V) is a known constant.

Optimization of Analytical Signal. Photoelectrochemical oxidation of organic compounds at the TiO_2 film electrode has been previously optimized by us for other applications.²⁴ To obtain the suitable experimental conditions for this particular analytical application, the system was further optimized.

The effect of applied potential bias was investigated. As applied potential bias was increased up to a critical value, a linear increase in the rate of oxidation was observed. Beyond the critical value, the rate of oxidation leveled off. These critical values of the potential bias were found to be between 0.08 and 0.18 V versus a $Ag/AgCl$ reference electrode depending on the light intensity and the concentration of organics in the solution. To ensure a sufficient potential bias under various conditions while at the same time minimizing the direct electrochemical reaction, a potential bias of +0.30 V was selected for all experiments.

The effect of light intensity was also investigated. It was found that the rate of oxidation was directly proportional to the applied light intensity. For a given sample, the time required for the exhaustive degradation is therefore directly proportional to the light intensity employed. For this reason, a high light intensity should be used. In practice, however, the high light intensity is often associated with stability problems, which may lead to the poor reproducibility. Hence, for this study, a relatively low light intensity of 6.6 mW cm^{-2} was selected.

The pH influence on the reaction rate and signal sensitivity was investigated. The results in this study showed that, within the pH range of 2–10, the photocurrents for solutions with organic compounds and without organic compounds remained almost unchanged with pH. This trend is similar to that previously found in the TiO_2 slurry system where photocatalytic degradation rate of organic compounds had little influence by pH changes.²⁶ Beyond the above pH range, the electrodes were found to be physically instable.

In the thin layer cell due to the very fine solution channel between working electrode and reference electrode, the large solution resistance often impairs the current signal. For our thin

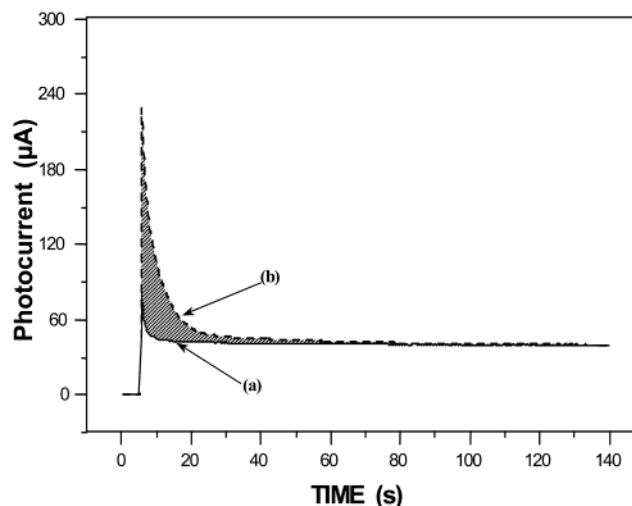


Figure 2. Photocurrent response of (a) 2 M $NaNO_3$ and (b) a 2 M $NaNO_3$ solution containing potassium hydrogen phthalate.

layer cell when 2 M $NaNO_3$ supporting electrolyte is used, a well-defined photocurrent signal can be obtained.

Measurement of Analytical Signal. Figure 2 shows a set of typical photocurrent–time profiles obtained during an exhaustive degradation of potassium hydrogen phthalate (KHP) in the thin-layer photoelectrochemical cell. Under a constant applied potential of +0.30 V, when the light was switched off, the residual current (dark current) was approximately zero. Upon illumination, the current increased rapidly before decaying to a steady value for both the blank and the sample solutions. For the blank (curve a), the photocurrent resulted purely from the oxidation of water, while photocurrent observed from the sample solution containing organics (curve b) consisted of two current components, one from photoelectrocatalytic oxidation of organics and the other from the oxidation of water, which was the same as the blank photocurrent. When all organics in the sample has been consumed, the photocurrent of the sample solution dropped to the same level as the blank.

For a given time period, the charge passed for both the blank and the sample solutions can be obtained by integration of photocurrents with time. The net charge originated from the oxidation of organics can be obtained by subtracting the charge of the blank from the charge of the sample, which is indicated as the shaded area in Figure 2. This net charge can then be used to quantify the COD value of a sample according to eq 3.

Validation of Analytical Principle. To validate the proposed methodology, a range of organic compounds including KHP, which is a standard for testing the standard COD method, was studied. The relationship between the net charge and the concentration of individual organic compound is given in Figure 3a. It can be seen that for all organic compounds investigated, the net charges obtained were directly proportional to the concentration. The slopes of the curves were found to be directly proportional to the number of electrons transferred to fully oxidize the organic compounds during the oxidative degradation. These evidences prove that the eq 2 is valid for such a type of photoelectrocatalytic degradation process.

Figure 3b was derived from Figure 3a by plotting the net charge against the theoretical COD values (see the data sets 1–8).

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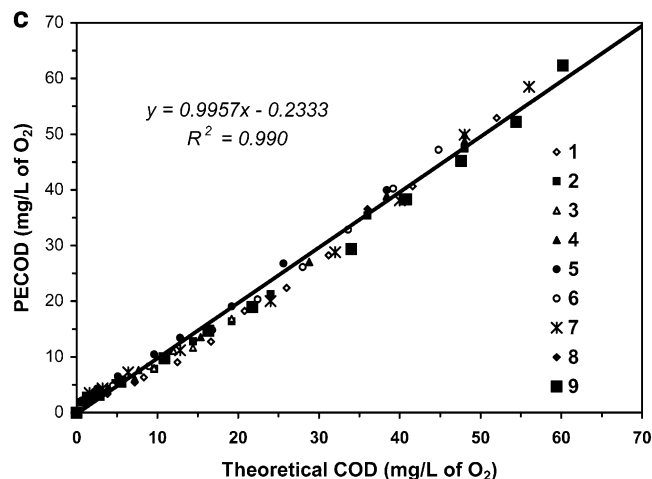
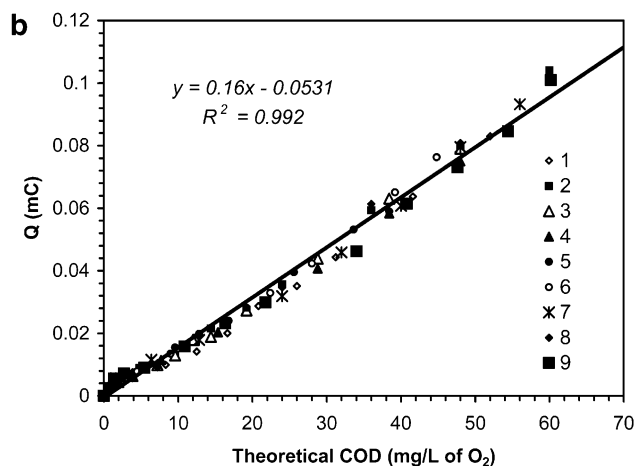
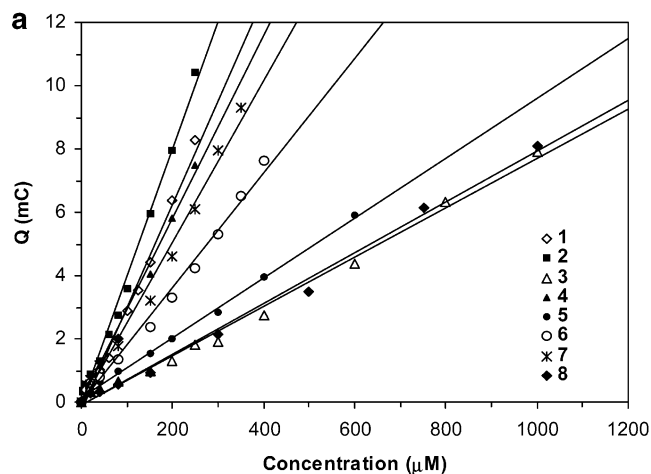


Figure 3. Validation of analytical principle: (a) the quantitative relationship between the net charge and the concentration of organic compounds; (b) the quantitative relationship between the net charge and theoretical COD; and (c) the correlation between the PECOD and theoretical COD. 1, *p*-chlorophenol; 2, potassium hydrogen phthalate (KHP); 3, methanol; 4, *D*-glucose; 5, malonic acid; 6, succinic acid; 7, glutaric acid; 8, glycine; 9, mixture of compounds 1–8 with equal COD concentration of each.

The data set 9 was obtained from a sample mixture containing equal COD concentration of all organics used for individual experiments. By converting the molar concentrations of individual organic compounds into the equivalent theoretical COD concentrations, we effectively normalized the data in Figure 3a into the

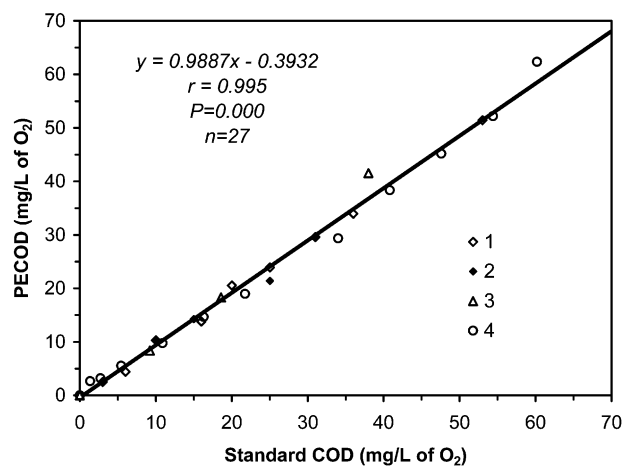


Figure 4. Correlation between the PECOD and the standard dichromate COD methods for the synthetic COD samples. 1, KHP; 2, GGA; 3, OECD; 4, mixture of compounds 1–8 in Figure 3 with equal COD concentration of each.

same measurement scale as shown in Figure 3b. Therefore, all compounds should fit into one linear line if the analytical principle proposed in equation 3 is correct. The result revealed that all compounds investigated including the mixture sample were fitted into a linear line with $R^2 = 0.992$, which proves the proposed analytical principle. The results also indicate that the system employed is capable of oxidizing different organic compounds uniformly. The slope of the curve can be used to evaluate the degree of photoelectrochemical catalytic degradation (oxidation). The theoretical slope of the curve equals $0.163 \text{ mC} [\text{mg L}^{-1} \text{O}_2]^{-1}$ can be calculated according to eq 3 by substituting $13.5 \mu\text{L}$ (the designed cell volume) for the volume of the thin layer cell. The experimental slope obtained was $0.160 \text{ mC} [\text{mg L}^{-1} \text{O}_2]^{-1}$, which is 98% of the theoretical slope value. This suggests that all organic compounds investigated were stoichiometrically oxidized to their highest oxidation form. These can be further evidenced by plotting the PECOD values against the theoretical COD values as shown in Figure 3c, where the line of best fit with the slope = 0.9957 and $R^2 = 0.990$ were obtained. This demonstrates that the method measures essentially the theoretical COD values.

The detection limit, linear range, and reproducibility were also evaluated. The evaluations of the detection limit and linear range were conducted using sample solutions containing different concentration of KHP in supporting electrolyte. The real detection limit of $0.20 \text{ mg L}^{-1} \text{COD}$ with linear range up to $200 \text{ mg L}^{-1} \text{COD}$ can be achieved under the experimental conditions employed. The calculated detection limit was $0.15 \text{ mg L}^{-1} \text{COD}$ with $S/N = 3$. The average noisy level was determined from nine blank electrolyte solutions. This detection limit is 20 times lower than that of previous reported.²⁷ It is to note that, with standard COD methods, the detection limit are from 4 to $10 \text{ mg L}^{-1} \text{COD}$ depending on the degradation method employed.¹ The reproducibility was evaluated by performing 17 replicate detections of a sample with the concentration of KHP equivalents to $15.0 \text{ mg L}^{-1} \text{COD}$. The relative standard deviation obtained was 0.87%.

Analysis of Synthetic and Real Samples. The applicability of the proposed principle was further validated using the standard

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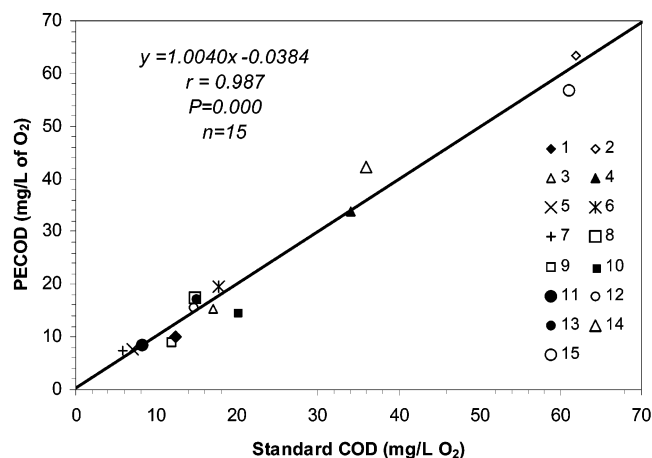


Figure 5. Correlation between the PECOD and the standard dichromate COD methods for the real sample measurements. 1–3 are the samples collected from wastewater treatment plants; 4–6 are the samples collected from sugar plants; 7–11 are the samples collected from brewery manufacturers and cannery manufacturers; 12–15 are the samples collected from dairy and food production plants.

COD test agent and three different types of other synthetic samples. Figure 4 shows the PECOD values measured with our method in comparison with the COD values of the same samples measured by standard dichromate COD method. The COD values obtained from the two methods agreed well as demonstrated by the high significant correlation between the two sets of COD values ($r = 0.995$, $P = 0.000$, $n = 27$) and the slope of the principal axis of the correlation ellipse of 0.9887. At 99% confidence interval, this slope was between 0.9400 and 1.0400.

The analysis of real samples was also carried out. These real samples were collected from various industrial sites and were again analyzed by both standard dichromate COD and newly developed PECOD methods. The correlation between the two methods is given in Figure 5. A highly significant correlation ($r = 0.987$, $P = 0.000$, $n = 15$) between the two methods was

obtained, indicating that the two methods agreed very well. More importantly, the slope of the principal axis of the correlation ellipse of 1.004 was obtained. This almost unity slope value suggests that both methods were accurately measuring the same COD value. Given a 95% confidence interval, this slope was between 0.9237 and 1.0916. This implies that we can be 95% confident that the true slope lies between these two values. Consider that there are analytical errors associated with both the PECOD and the standard method measurements and that these errors contribute to scatter on both axes, the strong correlation and slope obtained provides compelling support for the suitability of the PECOD method for measuring COD.

CONCLUSION

A novel COD analytical principle has been proposed and experimentally validated. The developed method has also been successfully applied to determinate the COD of a range of synthetic and real samples. The method is sensitive, which is capable of detecting as low as 0.2 mg L^{-1} COD. The method is also environmentally friendly, robust, rapid, and easy to be automated. It requires only 1–5 min to complete an assay and consumes very limited reagent (electrolyte only). More importantly, this method is a direct and absolute method. It does not require calibration standard. The method, in principle, measures the theoretical COD value due to the extraordinary high oxidation efficiency and accuracy of charge measurement. This method is free of the matrix effect due to the highly effective photoelectrochemical system employed that is capable of fully oxidizing a wide spectrum of organics in the sample exhaustively.

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