



Determination of chemical oxygen demand of nitrogenous organic compounds in wastewater using synergetic photoelectrocatalytic oxidation effect at TiO₂ nanostructured electrode

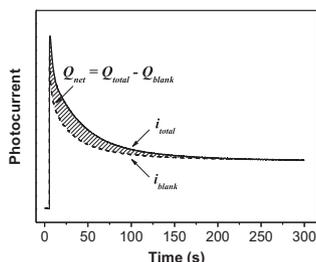
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HIGHLIGHTS

- ▶ A synergetic photoelectrocatalytic oxidation effect is observed at TiO₂ photoanodes.
- ▶ It assists the mineralization of nitrogenous organic compounds (NOCs).
- ▶ It facilitates the accurate measurement of COD of the NOCs-containing wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical oxygen demand (COD) is one of the most important parameters in water quality assessment and monitoring. The natural degradation of nitrogenous organic compounds (NOCs) in water requires significant amounts of oxygen. In the determination of standard COD however, NOCs are persistent compounds that cannot be completely oxidized even in the most oxidative chemical environments, i.e. the reaction media that contain high concentrations of dichromate in strong acid at high temperature. Consequently, the measured COD values of wastewater samples containing NOCs are commonly lower than theoretical COD values and do not reflect the actual oxygen demand of the water body. This problem is partially alleviated when the photoelectrochemical method for COD determination (PeCOD) based on nanostructured TiO₂ photoanode is utilized. To completely overcome this problem, a synergetic photoelectrochemical oxidation effect in thin layer cells is used to achieve complete oxidation of NOCs. This is done by the simple addition of a hydroxyl organic compound (i.e. glucose) into the test sample before the PeCOD measurement. Preliminary experimental results demonstrate that the synergetic PeCOD method provides an effective and reliable means to measure COD values of NOC-containing pollutants without the need for toxic or expensive reagents.

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1. Introduction

Oxygen, although poorly soluble in water, is essential for aquatic life and habitats [1]. Insufficient dissolved oxygen leads to the

sickness and death of aquatic organisms and may subsequently destroy the ecological environment. Decomposition of organic matter dramatically consumes dissolved oxygen, which has a substantial impact on the ecological system over both short and long time periods [1,2]. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are the two main indices used to assess oxygen demand. The BOD analysis measures the amount of biodegradable organic compounds in terms of the equivalent oxygen concentration required for their decomposition [3]. As COD determination (2–4 h) is simpler and faster than BOD₅ (5 days) [4],

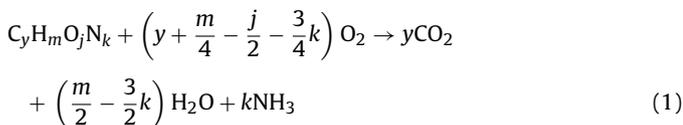
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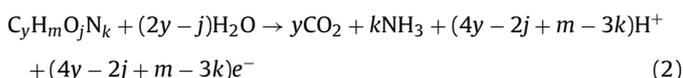
it is the preferred method for estimating the overall amount of the organic matters in wastewater.

The standard COD determination method requires a reflux process in acidic potassium dichromate solution at high temperature (148 °C) [5,6]. Typically, nearly all organic compounds can be fully oxidized to carbon dioxide with this method. The amount of oxygen required to oxidize a nitrogenous organic compound (NOC, $C_yH_mO_jN_k$) to carbon dioxide, ammonia and water is given by:



In spite of its strong oxidizing power, the dichromate solution cannot completely oxidize some NOCs, such as pyridine and its derivative compounds [7]. In natural environments, the NOCs are a large group of organic compounds that can be degraded by microorganisms [8–10]. Hence, the oxygen demand contribution from NOCs should be considered when determining actual oxygen demand. For example, urea [11–13], arginine [10], nicotinic acid and nicotinamide [8,9,14] can be biologically degraded in the environment with oxygen consuming. Using standard COD measurement, if NOCs can only be partially oxidized or cannot be oxidized at all, the COD values of samples containing NOCs will be underestimated. Consequently, the COD values obtained by the dichromate method are unable to reflect the real influence of NOCs on water bodies.

Recently, we developed a photoelectrochemical method (PeCOD) that detects the COD values in a simple, sensitive, accurate and rapid fashion [15–17]. With the PeCOD method, a wide spectrum of organic pollutants can be mineralized completely and indiscriminately at room temperature. This is attributed to the superior oxidation power of the UV illuminated TiO_2 photocatalyst. The general equation for complete mineralization of a NOC, $C_yH_mO_jN_k$, at a TiO_2 electrode surface can be represented by Eq. (2) [15]:



The electron transfer number (n) in the complete mineralization is equal to $4y - 2j + m - 3k$. The electron transfer amount (i.e., the charge) in this process can be quantified by electrochemical means and subsequently converted to COD concentration according to Faraday's law.

In this work, the COD determination of four NOCs, including urea, nicotinic acid, nicotinamide and arginine were investigated using the standard method and PeCOD method.



Urea is extensively used in industry and agriculture [18], with more than 90% of its production used as a fertilizer. Nicotinic acid, nicotinamide, and arginine serve important industrial functions, including solvents in pharmaceuticals and food industry additives [19]. These four NOCs are common in wastewaters. As previously mentioned, complete degradation of some NOCs cannot be achieved by the standard dichromate method [7]. Furthermore, despite the extraordinary oxidation power of the TiO_2

photocatalyst, the complete oxidation of some NOCs cannot be achieved by directly utilizing the PeCOD method. Herein, we propose to use a synergetic photoelectrocatalytic oxidation mechanism to improve the oxidation efficiencies of the NOCs in the PeCOD measurement, namely synergetic PeCOD measurement. In this method, a given amount of an oxidizable hydroxyl organic compound (e.g. glucose) is added to the test sample to allow the synergetic oxidation reaction to take place. The photoelectrocatalytic oxidation of urea was studied as an exceptional case in the PeCOD measurement process. A synergetic PeCOD measurement protocol and possible reaction mechanisms are proposed based on the experimental results. The use of the synergetic mechanism is expected to extend the applicability of the PeCOD technology.

2. Experimental

2.1. Chemicals and materials

Indium tin oxide (ITO) conducting glass slides ($8 \Omega \text{ sq.}^{-1}$) were supplied by Delta Technologies Ltd. Titanium butoxide (97%, Aldrich), urea, nicotinic acid, nicotinamide, arginine, glucose, sodium nitrate were purchased from Aldrich without treatment prior to use. All other chemicals were of analytical grade and purchased from Aldrich unless otherwise stated. High-purity deionized water (Millipore Corp., $18 M\Omega \text{ cm}$) was used in the preparation of all solutions.

2.2. Preparation of TiO_2 electrodes

The details of the TiO_2 colloid preparation have been published elsewhere [15,16]. Briefly, aqueous TiO_2 colloid was prepared by the hydrolysis of titanium butoxide [20]. The colloid for dip-coating slides contained 60 g L^{-1} TiO_2 solid and 18 g L^{-1} carbowax. The ITO slides were used as the electrode substrates and washed with acetone and water in turn to ensure their cleanliness. After the pre-treatments, the ITO slides were dip-coated in the TiO_2 colloidal solution. The coated electrodes were calcined at 450°C in air for 0.5 h in a muffle furnace; another layer was coated on the slide in the same way followed by calcination at 700°C in air for 2 h.

2.3. Apparatus and methods

All photoelectrochemical experiments were performed at 23°C in a thin-layer three-electrode photoelectrochemical cell with a quartz window for illumination [15]. The thin-layer cell consisted of three electrodes: a TiO_2 -coated working electrode, an Ag/AgCl reference electrode and a platinum mesh counter electrode. The thickness of the spacer was 0.1 mm, and the diameter of the quartz

lens was 5 mm. A 2.0 M $NaNO_3$ solution was used as the supporting electrolyte. A CS300 Electrochemical Workstation (Huazhong University of Science and Technology, Wuhan, China) coupled to a computer (DCNE, Dell Inc.) was used for the application of potential bias and recording potential and current signals. Illumination was carried out using a UV-LED (NCCU033, Nichia Corporation). The light intensity was controlled at 9.0 mW cm^{-2} which was measured at wavelength of 365 nm using a UV irradiance metre (Instruments

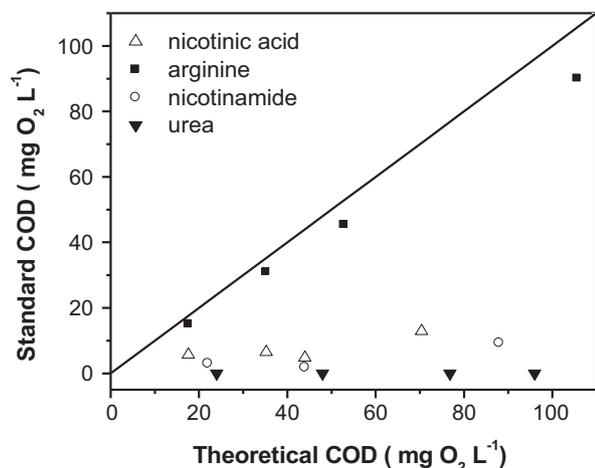


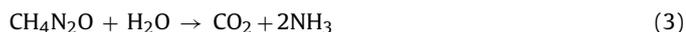
Fig. 1. Relationship between the measured standard COD values and the theoretical COD values of the individual NOCs samples. The line represents the ideal slope at 100% oxidation.

of Beijing Normal University). The standard COD values of all samples were measured with an EPA approved COD analyser (NOVA30, Merck).

3. Results and discussion

3.1. COD determination by the dichromate method

The COD values of the NOCs (i.e. urea, nicotinic acid, nicotinamide and arginine) at different concentrations were individually determined using the dichromate method. All the theoretical COD values were calculated based on the definition of COD (see Eqs. (1) and (2)) and the electron transfer numbers: $n=22$ for nicotinic acid, nicotinamide and arginine (when the oxidation reaction product is ammonia), and $n=16$ for urea (oxidation reaction product is nitrate). The measured standard COD values were well below their corresponding theoretical COD values (see Fig. 1). This demonstrated that none of the NOCs were completely oxidized using the dichromate method. In particular, the measured standard COD values and the oxidation percentages were zero for different COD concentrations of urea, which was consistent with the literature [21]. The standard dichromate method involves a digestion process in a highly acidic environment (9.7 M H_2SO_4) at 148 °C for 2 h. Under these conditions, urea was rapidly dissociated into carbon dioxide and ammonium [22]. This process involves no net electron transfer (see Eq. (3)). Moreover, it is well-established that ammonium cannot be further oxidized in the standard dichromate COD measurement process [5]. Consequently, urea does not contribute to the COD value when the standard dichromate method is used.



The relationship between the measured standard COD values and the theoretical COD values of nicotinic acid or nicotinamide was not linear, suggesting that the oxidation percentage varied with the concentration of nicotinic acid or nicotinamide (see Fig. 1). The average oxidation percentages of nicotinic acid and nicotinamide were only around 20% and 9.8%, respectively. Additionally, poor reproducibility was observed for both compounds, showing 24.6% and 22% RSD for three analyses, respectively.

In terms of oxidation percentage, arginine performed much better than the other three NOCs with an average oxidation percentage of 86.2% (see Fig. 1). In contrast with the other three NOCs, the measured COD values of arginine increased linearly with increasing theoretical COD values. A reproducibility of 1.5% RSD was obtained

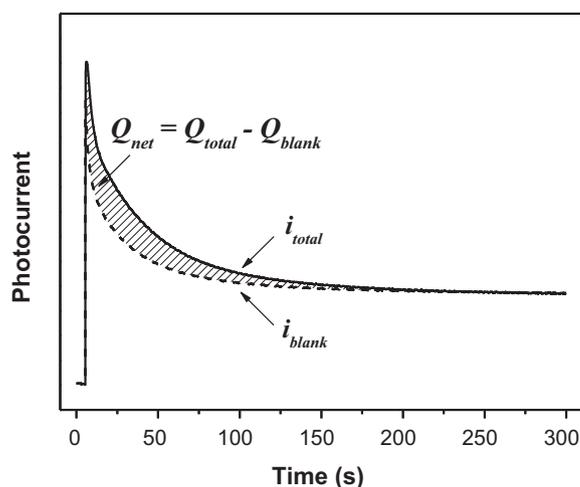


Fig. 2. Schematic diagram for photoelectrochemical determination of COD values: the dashed line and solid line represent photocurrent–time profiles of the i_{blank} and i_{total} , respectively.

from three analyses. Despite these better results, complete oxidation of arginine could not be achieved by the dichromate method.

In summary, the oxygen demands of the investigated NOCs were not fully reflected in the COD values measured by the standard dichromate method.

3.2. Direct PeCOD

In the direct PeCOD method [15] the photoelectrocatalytic degradation of organic matter was carried out in the thin-layer photoelectrochemical cell to minimize degradation time and maximize degradation efficiency. Faraday's law was used to quantify COD concentration by measuring the charge resulting from the photoelectrochemical degradation of organic matter (see Eq. (4)).

$$Q = \int i dt = nFVC \quad (4)$$

i represents the photocurrent from the oxidation of the organic compound; F , V and C are the Faraday constant, the sample volume and the concentration of the organic compound, respectively; n represents the electron number transferred during the photoelectrocatalytic oxidation, which is $4y - 2j + m - 3k$ (see Eq. (2)).

The detection principle of a typical PeCOD assay is displayed in Fig. 2. Under UV illumination, the photocurrent rapidly increased and then levelled off at a common steady value for both the blank and sample solutions. i_{blank} (dash line) originated from the photocatalytic oxidation of water while the i_{total} (solid line) resulted from the photocatalytic oxidation of organic compounds and water. The charge of blank (Q_{blank}) and the total charge of a sample (Q_{total}) were obtained by integrating the i_{blank} and i_{total} with the oxidation time, respectively. The net charge (Q_{net}) was obtained by deducting the Q_{blank} from the Q_{total} (see Eq. (5)). Q_{net} , generated from the complete degradation of organic compounds, can be used to subsequently quantify the COD value according to Faraday's law, since one oxygen molecule is equivalent to four transferred electrons (see Eq. (6)) [15].

$$Q_{\text{net}} = \int i_{\text{total}} dt - \int i_{\text{blank}} dt = Q_{\text{total}} - Q_{\text{blank}} \quad (5)$$

$$\text{COD}(\text{mg O}_2\text{L}^{-1}) = \frac{Q_{\text{net}}}{4FV} \times 32000 \quad (6)$$

The PeCOD values measured by the direct PeCOD method were plotted against the theoretical COD values of the individual NOCs

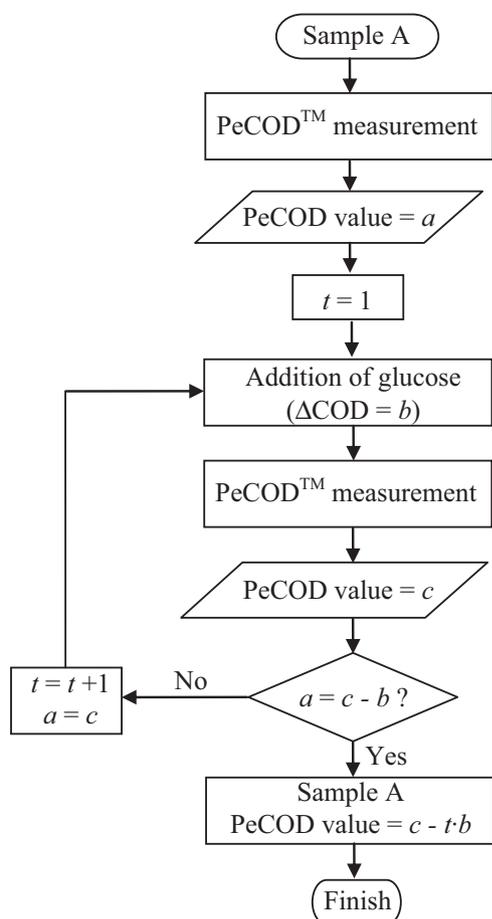


Fig. 6. Flow chart of the synergetic PeCOD determination procedure for aqueous samples containing NOCs.

dichromate solution, no significant improvement was observed when the NOC to glucose ratio was changed from 1:0 to 1:5 at different NOC concentrations. This suggests that the synergetic oxidation effect does not apply to the standard dichromate method. This is due to the oxidation mechanism of organic compounds in the dichromate method being different to that in the photoelectrocatalytic oxidation.

Real samples, such as dairy waste and food industry waste, potentially contain high concentration of NOCs. According to our previous work [15], the direct PeCOD method had excellent performance in the real sample analyses. This was due to the higher amounts of non-nitrogenous organic compounds (non-NOCs) in the real samples compared to NOCs. In fact, for real samples consisting of thousands of organic compounds but none or a small amount of NOCs, the synergetic photoelectrocatalytic oxidation could take place naturally, leading to accurate COD measurement without adding easily oxidizable organic compounds.

The protocol of the synergetic PeCOD method can be described in Fig. 6. For the samples containing a high ratio of NOCs to organic compounds, this method will become important for accurate measurements. This procedure can be applied to all types of water samples regardless of the NOC levels. In particular, to analyse the COD of a sample, the sample will be firstly subjected to the direct PeCOD measurement and a COD value of “*a*” obtained. A given concentration of glucose solution will then be added to the sample solution, resulting in the COD concentration increment of “*b*”. The mixed sample will then be again subject to the PeCOD measurement and a new COD value of “*c*” obtained.

If $a = c - b$, this suggests that the NOCs in the water sample do not affect the PeCOD measurement. In other words, the COD concentration for the sample is $c - b$.

If $a < c - b$, this suggests that addition of the glucose has resulted in the synergetic oxidation of NOCs in the sample. Further addition of glucose and PeCOD measurements will be needed to ensure sufficient glucose is provided for complete synergetic oxidation.

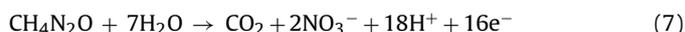
Logically, the times of glucose addition should be accumulated, which is achieved by the summator (i.e. $t = t + 1$). To determine the existence of the negative effect of NOCs on the COD value, a starting COD concentration should be set as a reference point before the addition of glucose. For $t = 1$, the starting COD concentration is *a*. For $t > 1$, mathematically, the addition of glucose should be taken into account, and thus *a* value is replaced with the last *c* value by using the iterator ($a = c$). The new *c* value will be obtained upon the new synergetic measurement. The results in Figs. 4 and 5 were obtained and monitored by this protocol.

3.4. Urea – an exceptional case

Urea is commonly treated as a special case in oxygen demand measurement because urea molecules contain a high ratio of nitrogen to carbon.

According to the oxidation reaction with O_2 (Eq. (1)), the electron transfer number is zero. In fact, urea does not contribute to COD value when standard dichromate method is used (see Fig. 1).

Similarly, according to the photoelectrochemical reaction (Eq. (2)), the electron transfer number shall be zero as well. In strong contrast, the direct PeCOD experimental results in Fig. 3 show that the charge values of the urea samples were over zero and increased linearly with the increase in urea concentration. This implies that the electron transfer takes place in the photoelectrocatalytic oxidation of urea. In fact, the photocatalytic oxidation could produce a higher percentage of NO_3^- than NH_3 in a traditional photocatalytic system [23]. It can be envisaged that the larger percentage of NO_3^- could be produced due to the enhanced oxidation power of the photoanode in the direct PeCOD method. If the amine functional groups in urea are oxidized to the highest oxidation state (i.e. nitrate), the overall mineralization equation in the thin-layer cell should be generalized as:



The electron transfer number for the mineralization of the urea is therefore 16. An oxidation percentage of 34% for urea can be obtained in the direct PeCOD measurement using the electron transfer number.

Fig. 7 shows the synergetic effect of glucose on the COD values and oxidation percentages of urea. The measured PeCOD values in Fig. 7 were the average of at least three analyses with a $RSD\% \leq 1\%$. The oxidation percentages were obtained by comparing the measured PeCOD values with the corresponding theoretical COD values. The oxidation percentage of urea was only about 30% at $12 \text{ mg } O_2 \text{ L}^{-1}$ urea when the direct PeCOD method was used (i.e. at $0 \text{ mg } O_2 \text{ L}^{-1}$ of glucose, Fig. 7). The oxidation percentage of urea increased to about 60% and 100% when the urea to glucose ratios changed from 1:1 to 1:2, respectively. At higher urea concentrations, e.g. 24 and $48 \text{ mg } O_2 \text{ L}^{-1}$, higher amounts of glucose were needed but similar oxidation percentages were obtained for the same urea to glucose ratios.

In summary, the oxidation of urea needs to be treated as an exceptional case in PeCOD measurement, following Eq. (7) rather than Eq. (3). The direct PeCOD method is able to partially oxidize urea, which is not observed in the standard dichromate method. The COD value obtained from the synergetic PeCOD reflects the contribution from the oxidation of urea to nitrate. Ultimately, regardless of the analytical methods used, the COD values must

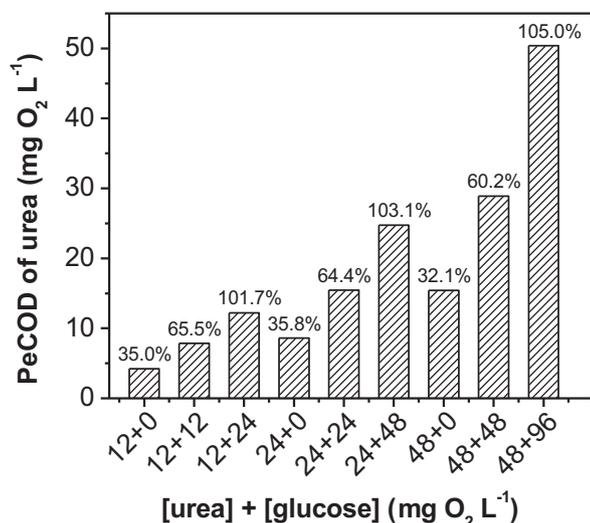


Fig. 7. The synergetic effect of glucose concentration on the photoelectrocatalytic oxidation percentage of urea using the synergetic PeCOD method. The oxidation percentages corresponding to the urea and glucose concentrations are indicated on the top of each column.

reflect the oxygen demand of organic compounds in water. Therefore, biological demand (BOD) is commonly considered as the best parameter to indicate the environmental impact of organic pollutants to water bodies. Clearly, in natural environment, NOC (such as urea) can be degraded directly or indirectly to NO_x^- (e.g., nitrification reaction) via different biological catalytic pathways, depending on the type of microorganisms [5]. In the standard BOD method, when the nitrification reaction is inhibited, the oxygen demand results are reported as carbonaceous biochemical oxygen demand (CBOD₅). When nitrification is not inhibited, the results are reported as BOD₅ [5]. In this sense, the PeCOD values obtained by the proposed synergetic PeCOD method shall be more comparable to the BOD₅ than to the CBOD₅. In other words, the PeCOD value obtained by this method might better reflect the oxygen demand of the water containing urea.

3.5. Mechanistic considerations

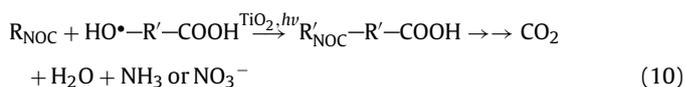
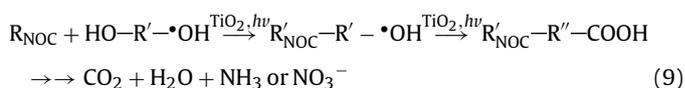
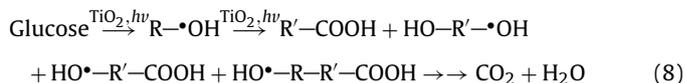
To explain the synergetic effect, we speculate on the following mechanism according to the related reaction mechanisms proposed in the literature. It is well established that photoholes are generated at the valence band at the TiO₂ surface under UV illumination. Thermodynamically, the photoholes (+3.1 V) are so powerful that they can mineralize almost all the organic pollutants in waters and wastewaters [24,25]. The mineralization of organic compounds in the thin layer cell involves diffusion, adsorption and multiple reaction steps [26–29]. Adsorption certainly plays an important role in this process. During this process, numerous intermediate radicals can be formed, and multiple steps for electron transfer will be involved [30]. The complete photoelectrocatalytic oxidation of a large variety of non-NOCs was obtained in the direct PeCOD measurements [15].

The degradation of NOCs is generally more complex than that of non-NOCs due to the multi-valence nature of the nitrogen element. The experimental results presented in Fig. 3 suggest that only partial oxidation can be achieved using the direct PeCOD measurement of the NOCs. This is probably due to the following two reasons. Firstly, the slow adsorption of this category of compounds causes the slow kinetics in the photoelectrocatalytic oxidation. Compared with the non-NOCs such as KHP [31], the adsorption of the NOCs and their oxidation intermediates on the TiO₂ surface is a relatively

slow process, leading to the slow kinetics process in the degradation of NOCs. Secondly, the reaction between NOCs and radicals often follows a slow kinetics process. Pelizzetti et al. [23,32] reported that the photocatalytic degradation rate of urea was slow due to the absence of extractable C–H bonds. In this case, $\bullet\text{OH}$ attack is forced at the $-\text{NH}_2$ moiety [32]. This attack, as the major reaction pathway, is very slow, and determines the slow degradation rate of urea [32]. In the suspension system reported by Pelizzetti et al., degradation of urea in a small reactor needs over 10 h [23]. In practice, the change of photocurrent originating from the degradation of the NOCs in the direct PeCOD measurement was so slow that the reaction was often considered as “finished” by the software and/or researcher, resulting in partial photoelectrocatalytic oxidation of NOCs and inaccurate COD measurement.

Glucose, as a prototype of polyhydroxyl carbohydrates and alcohols [33], can be easily oxidized. This is because glucose has abundant hydroxyl functional groups, and the OH groups closely associated with the photo-excited surface undergo easy oxidation [34]. In the direct PeCOD measurement process, glucose can be easily attacked by the photoholes and forms organic hydroxyl radicals ($\text{R}\bullet\text{OH}$) [34]. The ($\text{R}\bullet\text{OH}$) can further react with other hydroxyl radicals or organic compounds to form aldehydes ($\text{R}'\text{—CHO}$) and/or carboxylic organic compounds ($\text{R}'\text{—COOH}$) [34,35] that can be easily adsorbed and oxidized at the TiO₂ surface. Most importantly ($\text{R}\bullet\text{OH}$) can react with these intermediates and form $\text{HO}\text{—R}'\bullet\text{OH}$ and carboxylic hydroxyl radicals ($\text{HO}\bullet\text{—R}'\text{—COOH}$). These radicals with dual functional groups, i.e. hydroxyl radical and strong adsorption functional groups ($-\text{COOH}$), can subsequently attack other organic molecules and form $\text{HO}\bullet\text{—R}'\text{—COOH}$ that can be easily adsorbed on the TiO₂ surface and readily mineralized (see reaction scheme (8)). In other words, the dual functional radicals can act as carriers to bring non-adsorptive compounds to the TiO₂ surface for the mineralization reactions.

To initiate the synergetic effect, a sufficient amount of glucose needs to be added into the NOCs sample. In the presence of this kind of hydroxyl compound, the dual functional carriers such as $\text{HO}\text{—R}'\bullet\text{OH}$ and $\text{HO}\text{—R}'\bullet\text{COOH}$ can be obtained and react with the NOCs (i.e. R_{NOC}) following the reaction pathways as shown in reaction schemes (9) and (10), forming various adsorptive intermediates (e.g. $\text{R}'_{\text{NOC}}\text{—R}'\text{—COOH}$). These intermediates can be easily adsorbed on the TiO₂ surface. In other words, the NOCs can be carried by these carriers to the TiO₂ surface, which facilitates the oxidation of the NOCs to CO₂, H₂O, ammonia or nitrate.



4. Conclusion

Low oxidation percentages of NOCs in the standard dichromate method results in underestimations of COD values. The direct PeCOD method can partially alleviate this problem. By using the synergetic PeCOD method, the oxidation percentages of the NOCs were increased up to 100% when a sufficient amount of glucose was added to the NOC samples. The COD value of urea measured by the synergetic PeCOD reflects that urea can be oxidized to nitrate and might better reflect the oxygen demand of the water

containing urea. This is in strong contrast with the standard dichromate method, in which urea hydrolyses to ammonium and has no contribution to the standard COD value. This positive effect of the synergetic PeCOD method may be attributed to the additional oxidation pathways of the NOCs in the presence of glucose, and extended lifetime of free radicals due to the efficient and rapid photohole scavenging by glucose.

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