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Study on photocatalytic oxidation for determination of the low chemical oxygen demand using a nano-TiO_2–$Ce(SO_4)_2$ coexisted system

Yihao Chai, Hongchun Ding, Zhonghai Zhang, Yuezhong Xian,
Zhensheng Pan, Litong Jin*

Department of Chemistry, East China Normal University, ZhongShan Road North 3663, Shanghai 200062, China

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Abstract

A new photocatalytic system, nano-TiO_2–$Ce(SO_4)_2$ coexisted system, which can be used to determine the low chemical oxygen demand (COD) is described. Nano-TiO_2 powders is used as photocatalyst in this system. The measuring method is based on direct determination of the concentration change of Ce(IV) resulting from photocatalytic oxidation of organic compounds. The mechanism of the photocatalytic oxidation for COD determination was discussed and the optimum experimental conditions were investigated. Under the optimum conditions, a good calibration graph for COD values between 1.0 and 12 mg l^{-1} was obtained and the LOD value was achieved as low as 0.4 mg l^{-1}. When determining the real samples, the results were in good agreement with those from the conventional methods.

Keywords: Chemical oxygen demand (COD); Photocatalytic oxidation; TiO_2; Ce(IV); Synergistic reaction; Ultraviolet spectrophotometry

1. Introduction

Nowadays, with the increasingly severe environmental problem, environmental detection has become more and more important and is directly related with economic profit. The organic matter content in wastewater can be determined by using a variety of analytical methods such as total organic carbon (TOC), biological oxygen demand (BOD) or chemical oxygen demand (COD) [1]. In recent years, total organic carbon (TOC) has been of great interest in different environmental and industrial settings because some modern, automated TOC analyzers can offer interesting characteristics, especially at the lower concentration range [2,3]. However, the data obtained are sum parameters, which are not enough to explain all the results and show a poor correlation with the actual oxygen demand of aqueous samples. Moreover, determination of TOC relies on specific instruments, which is rather expensive [4,5]. So there emerges the need for an independent method to control the organic compound concentration. It seems that the COD might give the right answer, which refers to the oxygen required for complete oxidation of a wastewater sample, and is a widely used parameter in controlling the degree of pollution in water and managing effluent quality [6]. Thus, COD is most widely used in the characterisation of polluting aqueous effluents and can be used as a complement to TOC.

Usually, for COD determination, the organic matter contained in a given sample of water is oxidized by adding a known excess of a strong oxidant. After a refluxing digestion step, the remaining excess of oxidant is titrated [7]. Although the conventional method for COD determination displays exactitude and good reproducibility, it also has some serious drawbacks [8], for example: (1) The procedure is time-consuming, which totally takes around 2 h for oxidation and titration. In the operation of a wastewater treatment plant, it is hard to operate with delay times between sampling and results of more than 2 h. Meanwhile, the 2 h oxidation and titration requires large amount of water and electric power, which is obviously uneconomical for water treatment plant or

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* Corresponding author. Tel.: +86 21 62236267; fax: +86 21 62236267.
E-mail address: ltjin@chem.ecnu.edu.cn (L. Jin).

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environmental detection department. (2) Its accuracy depends on operator's skill. (3) It requires expensive (Ag_2SO_4) and toxic ($HgSO_4$) reagents, which will increase the cost and bring about secondary pollution. (4) When determining the low COD values (<30 mg l^{-1}), the conventional method using potassium dichromate has large error. Thus, it is not suitable for the determination of the tap water, spring water and reservoir water.

The above discussion clearly indicates the major limitations of both standard COD methodologies during the degradation process. These limitations could be surmounted if a more effective degradation method is employed. Recently the use of a microwave heating system, which has gained a wide attention, has been largely employed in the chemical digestion step [9–11]. Although this method displays some advantages such as expeditiousness and cleanliness, it still needs some further improvements in the real sample determination. For instance, reagents as Ag_2SO_4 and $HgSO_4$ are still employed in the method although their amount has been cut. It is able to detect the COD down to 10 mg l^{-1} but its reproducibility and accuracy are not as good as those when determining the high COD. In order to obtain the high oxidation efficiency, high temperature is required, which may cause safety problem.

The recently developed photoactive TiO_2 nanomaterial combined with photocatalytic technologies provide an alternative means for organic matter degradation because the photogenerated holes in an illuminated TiO_2 semiconductor are very powerful oxidizing agent (+3.2 V) that is capable of oxidizing nearly any organic species found in natural waters and wastewaters [12–14]. However, the high recombination of the photogenerated electron/hole pairs may be a disadvantage for its application. Addition of oxidants is a theoretically efficient way to inhibit the recombination.

In this paper, we attempt to introduce Ce(VI) into TiO_2 photocatalytic system as an electron scavenger, and thus, a new COD measurement method using a nano-TiO_2–$Ce(SO_4)_2$ coexisted system is proposed. The measuring principle is based on the direct determination of concentration change of Ce(IV) during photocatalytic oxidation of organic compounds. The proposed method, which only needs 2 min for photocatalytic oxidation and has a limit of detection (LOD) as 0.4 mg l^{-1}, is a fast, accurate and sensitive method. In addition, this method does not require expensive and toxic reagents. The values obtained can reliably be correlated with the COD values obtained by the conventional methods.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade (Shanghai Chemical Reagent Company).

A standard solution of D-glucose, corresponding to 1000 mg l^{-1} COD, was prepared by dissolving 0.9372 g of D-glucose in 1 l of distilled water. Different COD values were obtained through appropriate dilutions and were proved by the conventional standard method (potassium permanganate method).

A 8.0862 g amount of cerium(IV) sulphate was dissolved in 1 l of distilled water containing 50 ml of sulphuric acid. The final concentration in the reagent solution was 0.02 mol l^{-1}.

P-25 TiO_2 was obtained from the Degussa Corporation and used as received. It has been reported to be a nonporous 70:30 anatase:rutile mixture, with a BET surface area of ca. $55 \pm 15\ m^2\ g^{-1}$ and crystallite size of 30 nm in 0.1 μm diameter aggregate [15]. KOH and H_2SO_4 were used to adjust pH of the reaction solution.

2.2. Device

A bath reactor system was shown in Fig. 1, which was used to perform the photocatalytic reaction. The reaction mixture inside the reactor was maintained in suspension state by means of a magnetic stirrer. A UV irradiator with a 11 W UV lamp (Shanghai Jinguang Lamps Factory, central wavelength: 253.7 nm), placed in the center of the reactor, was used as the UV source. The reactor was equipped with a water jacket to maintain a constant temperature.

The absorbance change caused by a decrease in Ce(IV) concentration was measured by a UV spectrophotometric detector (Varian Corp., Model Cary 50) and operated at 320 nm.

An ORP electrode (Shanghai Sanxin Instrumental Factory) was used to determine the oxidation–reduction potential of Ce(IV).

2.3. Experimental procedure

The sample solution, Ce(IV) solution and a fixed amount of TiO_2 powders were added to the reactor. The total volume

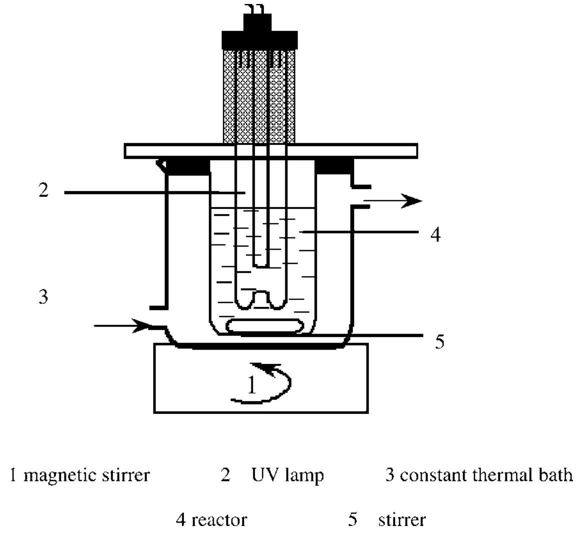

Fig. 1. Schematic diagram of the photocatalytic reactor.

of reaction solution was maintained at 40 ml for each experiment. In order to maintain a constant temperature, the reactor was water-jacketed. A magnetic stirrer was used through the experiment. The pH of the solution was adjusted to 1.2 with KOH and H_2SO_4 and monitored by a Kyoto AT-400 autotitrator. Photocatalytic oxidation of the organic compounds occurred under the illumination of the UV lamp, accompanying an decrease of Ce(IV) concentration. After 2 min oxidation reaction, the aqueous samples were centrifuged by a centrifugal presvac DCS-16 RV. The absorbance of Ce(IV) was determined at 320 nm with a UV spectrophotometric detector. All measurements were repeated three times.

For preparing a COD calibration, different volume of glucose was stepwisely added to the reactor and the corresponding absorbance of Ce(IV) was determined. Then, the COD calibration graph of the absorbance of Ce(IV) (A) versus COD was obtained.

3. Results and discussion

3.1. Measurement principle

The photocatalytic method is based on the special structure of the semiconductor (such as TiO_2), characterized by a filled valence band and an empty conduction band. When it accepts a photon with an energy equal to or greater than the band gap, an electron is promoted to the conduction band, leaving behind a positive hole in the valence band [16]. The valence band holes are powerful oxidants, which can degrade organic compounds in aqueous solution. Ce(IV) acts as a scavenger of photogenerated electrons and is reduced to Ce(III). The whole reaction is shown as follows:

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{1}$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$$^{\bullet}OH + R \rightarrow \cdots \rightarrow CO_2 + H_2O \tag{3}$$

$$h^+ + R \rightarrow \cdots \rightarrow CO_2 + H_2O \tag{4}$$

$$h^+ + e^- \rightarrow h\nu\,(\text{or heat}) \tag{5}$$

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \tag{6}$$

where h is a hole and R is an organic compound.

Accepting the photogenerated electrons, Ce(IV) can reduce the recombination of the photogenerated electrons and holes (reaction (5)), and thus, accelerate the reaction rate of (3) and (4).

Theoretically, with these holes and electrons, organic compounds are oxidatively degraded, accompanying the concentration change of Ce(IV). This indicates that COD value is proportional to the reductive amount of Ce(IV).

Fig. 2 demonstrated the oxidative ability of the nano-TiO_2–$Ce(SO_4)_2$ coexisted system. Under the settled conditions, glucose oxidation efficiency of the nano-TiO_2–$Ce(SO_4)_2$ coexisted system, $Ce(SO_4)_2$ system and TiO_2 system were studied, separately.

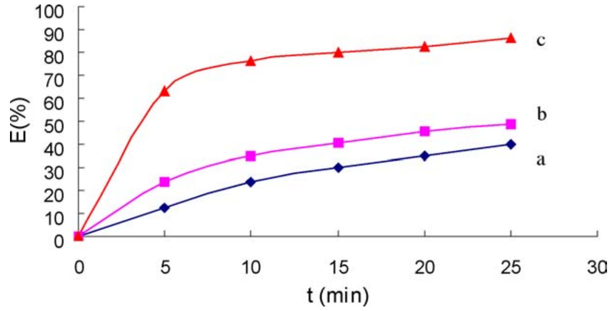

Fig. 2. Glucose oxidation efficiency (E) with different reaction conditions. Conditions: (a) pH 1.2, T 40 °C, TiO_2 0.5 mg ml^{-1}, COD 5 mg l^{-1}; (b) pH 1.2, Ce(IV) 1×10^{-3} mol l^{-1}, T 40 °C, COD 5 mg l^{-1}; (c) pH 1.2, Ce(IV) 1×10^{-3} mol l^{-1}, T 40 °C, TiO_2 0.5 mg ml^{-1}, COD 5 mg l^{-1}.

From Fig. 2, glucose oxidation efficiency after 5 min are 12.2, 23.5 and 63.4% in TiO_2 system, $Ce(SO_4)_2$ system and the nano-TiO_2–$Ce(SO_4)_2$ coexisted system, separately. Therefore, it can be concluded that the nano-TiO_2–$Ce(SO_4)_2$ coexisted system can largely enhance the oxidation efficiency of the organic compounds, and thus, the determination time is shortened and the sensitivity is increased.

3.2. Optimization of operation conditions

3.2.1. Influence of pH value

The effect of pH on the photocatalytic oxidation of organic compounds using Ce(IV) as an electron scavenger was investigated. The pH window is very narrow and is limited to $pH < 2$, in which Ce^{4+} ions exists in some well-defined and stable state. Lowering the pH results in the shift of the redox potential of the $E_{Ce^{4+}/Ce^{3+}}$ couple (Pt–Ag/AgCl electrode) to more positive potentials, which means that the photocatalytic oxidation ability of organic compounds increases with a decrease in the pH. The reason for this is Ce^{4+} would undergo hydrolysis and sulphate complexation under high pH conditions [17–23]. Values of stepwise stability constants of Ce(IV) are shown as following [21,22]:

$$Ce^{4+} + HSO_4{}^- \rightarrow CeSO_4{}^{2+} + H^+ \quad (K_1 = 3500),$$

$$CeSO_4{}^{2+} + HSO_4{}^- \rightarrow Ce(SO_4)_2 + H^+ \quad (K_2 = 200),$$

$$Ce(SO_4)_2 + HSO_4{}^- \rightarrow Ce(SO_4)_3{}^{2-} + H^+ \quad (K_3 = 20)$$

Meanwhile, the use of high acid concentration causes the reaction of the interfering compounds, such as chloride, with oxidizing agents. Consequently, pH 1.2 was selected for further experiments.

3.2.2. Selection of the electron scavenger and its initial concentration

The conventional method for COD determination is manual and is based on titration of the samples with a toxic reagent such as potassium permanganate or potassium dichromate. This type of standard manual method is time consuming and its accuracy depends on operator's skill. In order to reduce the chloride interference, mercury sulphate and/or silver sulphate is added, which is toxic and will cause the secondary pollution. While determining the low COD values ($<10\,\mathrm{mg\,l^{-1}}$), the error cannot be neglected [24].

Much effort has been devoted to the improvement and alteration of the standard manual methods [25–31]. However, the main problems still to be resolved are the toxic effluent produced during the COD determination and the complicated operating conditions necessary to obtain a high degree of sample oxidation. Consequently, an alternative method for COD determination, if it can result in a high degree of sample oxidation under milder conditions, is most desirable.

Wide attention has been paid to the photocatalytic degradation of the organic compounds by using nano-TiO_2, which has been applied to the determination of the COD value [32,33]. However, suitable oxidizing agent should be selected as the electron scavenger because of the easy recombination of the photogenerated electrons and holes. To achieve this, cerium(IV) sulphate is chosen as a suitable candidate and appeared to have a great promise.

The standard redox potential of the Ce^{4+}, $MnO_4{}^-$ and $Cr_2O_7{}^{2-}$ are shown as following:

$$Ce^{4+} + e^- \rightarrow\ Ce^{3+} \quad (E^\theta =\ 1.61\,\mathrm{V}) \tag{7}$$

$$MnO_4{}^- + 8H^+ + 5e^- \rightarrow\ Mn^{2+} + 4H_2O$$
$$(E^\theta =\ 1.51\,\mathrm{V})\,(\mathrm{V\ versus\ NHE}) \tag{8}$$

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (E^\theta = 1.33\,\mathrm{V}) \tag{9}$$

According to their redox potential, Ce(IV) is much stronger than Cr(VI) and Mn(VII) as an oxidizing agent. Therefore, it is much faster for the nano-TiO_2–$Ce(SO_4)_2$ synergic system to degrade the organic compounds, which only takes 2 min for photocatalytic oxidization.

Fig. 3 illustrates the absorption spectra of Ce(IV) and Ce(III); maximum absorption of Ce(IV) is found at 320 nm. At this wavelength, the absorption of Ce(III) is negligible compared to that of Ce(IV). Ce(III) has an absorption peak at around 250 nm, which will be influenced by the absorption spectrum of Ce(IV). That's why we cannot use the change of the Ce(III) concentration as the quantitative base.

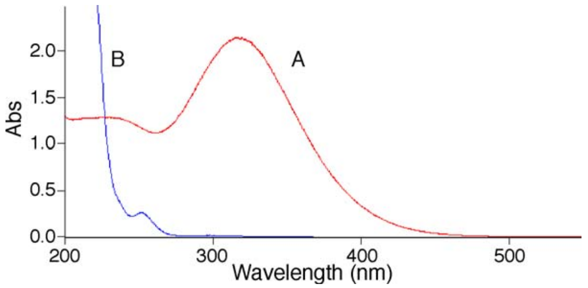

Fig. 3. Absorption spectra of (A) $1.0\times10^{-4}\,\mathrm{mol\,l^{-1}}$Ce(IV), (B) $1.0\times10^{-4}\,\mathrm{mol\,l^{-1}}$Ce(III) in pH 1.2 sulphuric acid solution.

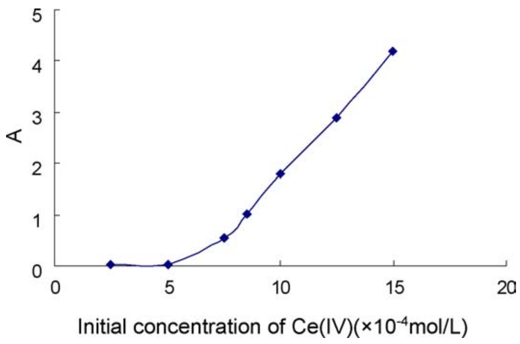

Fig. 4. Effect of the initial concentration of Ce(IV) on the photocatalytic determination of COD, Conditions: pH 1.2; TiO_2 $0.5\,\mathrm{mg\,ml^{-1}}$; T 40 °C; t 2 min; COD $5\,\mathrm{mg\,l^{-1}}$.

The effect of the initial concentration of Ce(IV) on the photocatalytic determination of COD by the UV/TiO_2 process at pH 1.2 was studied. The results are shown in Fig. 4. The absorbance increases with the increasing concentration of Ce(IV) and becomes markedly for higher concentration. However, if the concentration is too high, it will go beyond the range of the UV absorption. So $1.0\times10^{-3}\,\mathrm{mol\,l^{-1}}$ was selected as the initial concentration of Ce(IV).

3.2.3. *Dosage of the photocatalyst TiO_2*

The effect of various amounts of TiO_2 was determined using a COD $5\,\mathrm{mg\,l^{-1}}$ standard water sample at a fixed pH value of 1.2. The change of the absorbance of Ce(IV) with various TiO_2 dosages is shown in Fig. 5. It indicates that the oxidation rate of organic compounds increases correspondingly with the addition of TiO_2 dosage up to $0.5\,\mathrm{mg\,ml^{-1}}$. Then, the increase gradually approaches a limiting value for higher dosages of TiO_2. This can be explained by the high TiO_2 dosage decreasing the penetration of light, and thus, reducing the effectiveness of the photocatalytic oxidation.

3.2.4. *Influence of chloride*

Chlorides represent the most important interference in COD determination, since they are amenable to oxidation when no mercury(II) sulphate and/or silver sulphate is added

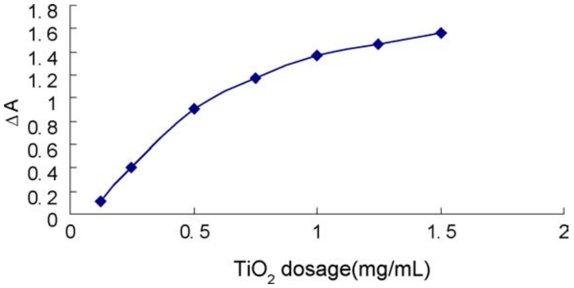

Fig. 5. Effect of TiO_2 dosage on the photocatalytic determination of COD. Conditions: pH 1.2; Ce(IV) $1\times10^{-3}\,\mathrm{mol\,l^{-1}}$; T 40 °C; t 2 min; COD $5\,\mathrm{mg\,l^{-1}}$.

Table 1
Comparison of COD values (mg l^{-1}) obtained by the proposed method with those by the conventional (COD_{Mn}) method

Sample	COD values (mg l^{-1})			
	This method	R.S.D. (%) ($n = 7$)	COD_{Mn}	R.S.D. (%) ($n = 7$)
Spring1	1.61	3.1	1.90	2.7
Spring2	1.88	1.5	2.18	1.3
Tap water	5.05	2.4	3.93	1.9
Reservoir water	5.34	2.8	4.16	3.3
Estuary region of Yangtze River	13.82	1.9	12.82	2.1
West Lake	15.50	0.9	14.15	1.1
Xiuzhu Lake	15.14	2.6	15.03	3.2

[25–27,29]. Here, the interference from chloride was investigated under the optimum operation conditions using the standard solution (5 mg l^{-1} COD) containing chloride levels between 0 and 1000 mg l^{-1}. It is found that up to 1000 mg l^{-1} Cl^- does not show any effect on the results without the need for the addition of mercury(II) sulphate and silver sulphate, when Ce(IV) is used as an oxidant.

3.3. Calibration graphs for COD and the limit of detection (LOD)

Using glucose at various concentrations, a calibration graph was prepared based on the following mechanism [34]:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Under the optimum conditions described above, the calibration graph of the absorbance of Ce(IV) (A) versus COD was linear in the range of 1.0–12 mg l^{-1}. A linear regression at a 95% confidence level of the values provided by the proposed method gave the following equation:

$$A = (0.2384 \pm 0.0016)\,\mathrm{COD} + (0.0293 \pm 0.0284)$$

$$(r = 0.9967, n = 7)$$

According to IUPAC, the limit of detection (LOD) was determined from three times the standard deviation of the blank signal (3σ, $n = 7$) as 0.4 mg l^{-1}. The low LOD can be explained by the enhancement of the photocatalytic oxidizing efficiency of the organic compounds in the water because of the strong ability of scavenging the electron of Ce(IV).

3.4. Determination of real samples

Real samples taken from various types of groundwater were analyzed by the present method. If the COD value of the real sample is over 12 mg l^{-1}, the sample can be diluted before determination.

The results for seven groundwater samples obtained by the proposed method compared with those by the standard manual method using potassium permanganate were given in Table 1 and the correlation was satisfactory. The regression equation and correlation coefficient were $y = 1.0461x + 0.2455$ and $r = 0.9940$ ($n = 7$), respectively, where y and x denoted the COD values obtained by the present method and the standard manual method, respectively. The comparison shows that the proposed method is in good agreement with the standard method and has a promising application prospect.

4. Conclusion

The purpose of this work is to develop a new method using nano-TiO_2–$Ce(SO_4)_2$ synergic system for monitoring COD. In this system, where $Ce(SO_4)_2$ is stoichiometrically involved, $Ce(SO_4)_2$ can easily accept photo-generated conduction band electrons and enhance the ability of photocatalytic degradation of organic compounds. Therefore, the COD of a given sample can be assessed by tracing the change of the concentration of Ce(IV). The optimization of operation conditions was studied. Under the mild conditions, a good calibration graph for COD values between 1.0 and 12 mg l^{-1} was obtained. When determining the real samples, the present method displays rapidness, simplicity, and high sensitivity. Additionally, results obtained by the method were in good agreement with the values obtained by the conventional method. Thus, it showed a promising prospect for determining the low-COD values of the ground waters.

Acknowledgements

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