

# Study on photocatalytic oxidation for determination of the low chemical oxygen demand using a nano-TiO<sub>2</sub>–Ce(SO<sub>4</sub>)<sub>2</sub> coexisted system

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## Abstract

A new photocatalytic system, nano-TiO<sub>2</sub>–Ce(SO<sub>4</sub>)<sub>2</sub> coexisted system, which can be used to determine the low chemical oxygen demand (COD) is described. Nano-TiO<sub>2</sub> 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<sup>-1</sup> was obtained and the LOD value was achieved as low as 0.4 mg l<sup>-1</sup>. When determining the real samples, the results were in good agreement with those from the conventional methods.

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## 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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environmental detection department. (2) Its accuracy depends on operator's skill. (3) It requires expensive ( $\text{Ag}_2\text{SO}_4$ ) and toxic ( $\text{HgSO}_4$ ) reagents, which will increase the cost and bring about secondary pollution. (4) When determining the low COD values ( $<30 \text{ mg l}^{-1}$ ), 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  $\text{Ag}_2\text{SO}_4$  and  $\text{HgSO}_4$  are still employed in the method although their amount has been cut. It is able to detect the COD down to  $10 \text{ mg l}^{-1}$  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  $\text{TiO}_2$  nanomaterial combined with photocatalytic technologies provide an alternative means for organic matter degradation because the photogenerated holes in an illuminated  $\text{TiO}_2$  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  $\text{TiO}_2$  photocatalytic system as an electron scavenger, and thus, a new COD measurement method using a nano- $\text{TiO}_2$ - $\text{Ce}(\text{SO}_4)_2$  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  $0.4 \text{ mg l}^{-1}$ , 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  $1000 \text{ mg l}^{-1}$  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  $0.02 \text{ mol l}^{-1}$ .

P-25  $\text{TiO}_2$  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.  $55 \pm 15 \text{ m}^2 \text{ g}^{-1}$  and crystallite size of 30 nm in  $0.1 \mu\text{m}$  diameter aggregate [15]. KOH and  $\text{H}_2\text{SO}_4$  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  $\text{TiO}_2$  powders were added to the reactor. The total volume

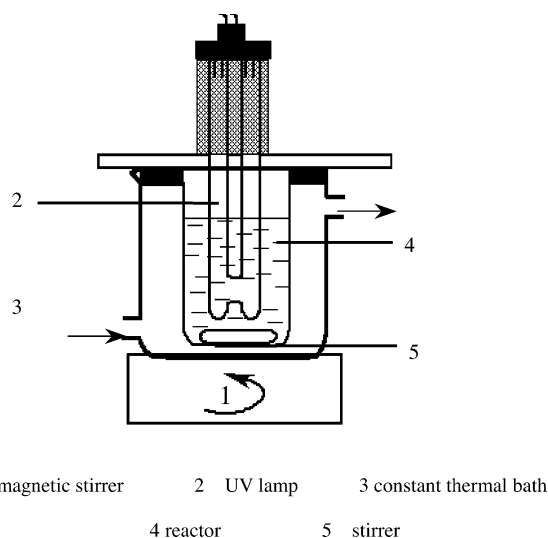


Fig. 1. Schematic diagram of the photocatalytic reactor.

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