Sensors and Actuators B 188 (2013) 280–285

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A visible light assisted photocatalytic system for determination of chemical oxygen demand using 5-sulfosalicylic acid *in situ* surface modified titanium dioxide

Shunxing Li*, Fengying Zheng, Shujie Cai, Wenjie Liang, Yancai Li

Department of Chemistry and Environmental Science & Fujian Province Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, China

ARTICLE INFO

Article history:
Received 27 February 2013
Received in revised form 13 June 2013
Accepted 30 June 2013
Available online 12 July 2013

Keywords:
Chemical oxygen demand
Visible light assisted photocatalytic oxidation
Titanium dioxide
Surface modification

ABSTRACT

Titanium dioxide (TiO_2) nanoparticles were *in situ* surface modified by the chemisorption of 5-sulfosalicylic acid as non-sacrificial organics and then used as a visible light active photocatalyst (5-SA-TiO_2). Based on the photodegradation of organic pollutants, a new system, 5-SA-TiO_2–$KMnO_4$, was used for the first time for the determination of chemical oxygen demand (COD). A linear correlation was observed between the amount of oxidizable dissolved organic matter and the amount of MnO_4^- consumed by the coupled reduction process. Thus, COD could be determined by the depletion of MnO_4^-. After TiO_2 was surface modified by 24.82 μg/mg of 5-SA, the working calibration range was extended from 2–12 mg/L and 50–300 mg/L to 0.3–400 mg/L and the disadvantages of pure TiO_2 for COD detection techniques were overcome, including UV irradiation and low oxidation percentage. Without any sample pretreatment and toxic reagents, the COD values of nature water and real wastewater could be successfully determined by achieved technique. Excellent agreement between our proposed method and conventional dichromate method was achieved.

1. Introduction

Chemical oxygen demand (COD) is an important index for the assessment of organic pollution in aqueous system. The conventional $K_2Cr_2O_7$ method for COD determination is accurate, reliable and reproducible, however, this method has some drawbacks, including low detection sensitivity, long time consumption (2–4 h), incomplete oxidation and mineralization, the need for toxic reagents (Cr and Hg), and secondary pollution [1,2]. Therefore, developing a rapid, simple, environmental friendly, and accurate method for COD detection is still a challenge in environmental and analytical field.

Many alternative oxidation methods have been investigated, including microwave-assisted oxidation, ultrasound-assisted oxidation, UV-O_3 oxidation, electrocatalytic oxidation, and titanium dioxide (TiO_2) photocatalytic oxidation [2]. Among these, photocatalytic oxidation approach is an effective degradation method because of its high efficiency, low energy consumption, simple operation, mild reaction conditions, and little secondary pollution [3]. TiO_2 nanoparticles are the most widely used photocatalysts for their advantages such as low cost, long-term photochemical stability, and nontoxicity [4,5]. The sensing application of TiO_2 is first demonstrated by Fox and Tien [6] who used a Ti/TiO_2 electrode to detect aniline in a high performance liquid chromatography (HPLC) system in 1988. In 2000, the photocatalytic degradation reaction of UV illuminated TiO_2 is utilized for the first time for the determination of chemical oxygen demand (COD) [7]. TiO_2 nanomaterials have been used as chemical sensor for COD determination [8]. But the photodegradation efficiency of TiO_2 is limited by: (a) its wide band-gap, (b) weak light absorption properties, (c) the extremely low coverage of organic maters on the photocatalyst, (d) its high degree of electron–hole recombination under photoexcitation, and (e) the sluggish reduction and oxidation rates on the surface [5,9–12]. So, the direct use of TiO_2 for COD detection is limited by UV irradiation, low oxidation percentage, and narrow linear range (less than 20 mg/L) [13,14]. To overcome above drawbacks, TiO_2 should be modified for improving its surface properties, adsorption ability, and photodegradation activity. Fluorinated-TiO_2 and nano-ZnO/TiO_2 composite film have been used as photocatalysts for COD determination, its working calibration range has been improved as 0.1–280 mg/L and 0.3–10.0 mg/L, respectively [15,16], but it cannot fit the requirement of COD determination in wastewater samples for its limited linear range.

TiO_2 could be surface modified by Fe(III)-porphyrin [17], ascorbic acid [18], arginine [19], triethylamine [20], 2-hydroxyethanesulfonic acid [21], folic acid [22], tartaric acid

---

* Corresponding author. Tel.: +86 596 2591395; fax: +86 596 2591395.
E-mail addresses: lishunxing@munu.edu.cn, shunxing_li@aliyun.com (S. Li).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.06.105

[23], isocyanate [24], S-1-dodecyl-S′-(α, α′-dimethyl-α″-acetic acid) trithiocarbonate [25], and aluminum phthalocyanine [26]. Above-mentioned modification methods are based on physical adsorption of organic molecules onto TiO_2 surface. The modified layer is easily desorbed or decomposed under the photoirradiation, *i.e.*, these surface modified agents are sacrificial organics. The photocatalytic activity is decreased during the reaction process [21,24]. Furthermore, the surface coverage of organic pollutants on the TiO_2 is still poor and the modification procedure is time-consuming, high cost, and complicated.

Aromatic compounds are common pollutants, especially as priority pollutants [5]. The affinity interaction between TiO_2 and aromatic pollutants is important for the photocatalytic activity [5]. Herein, TiO_2 nanoparticles are *in situ* modified by chemisorption of 5-sulfosalicylic acid (5-SA) with different surface modification levels and the catalysts prepared in this way are denoted as 5-SA-TiO_2. Through a proposed bidentate six-member ring interaction between 5-SA and —OH groups on TiO_2 surface, surface modification could be stable during the process of photodegradation and adsorption [10]. After 5-SA-TiO_2 is reused 10 times, the stability of surface modification is proved by its IR spectra, so 5-SA is used as non-sacrificial organics. The photocatalytic activity of 5-SA-TiO_2 is tested by the photodegradation of potassium hydrogen phthalate (KHP). The $KMnO_4$ is introduced into the photocatalytic system as an electron scavenger. Thus, a novel method for COD measurement is proposed, using 5-SA-TiO_2–$KMnO_4$ system. The influence of surface modification level on the photodegradation of KHP and the analytical performance of COD determination is discussed.

2. Materials and methods

2.1. Reagents

A standard solution of KHP, corresponding to 1000 mg/L COD, was prepared by dissolving 0.8502 g KHP in 1000 mL of water. A solution of 25 mmol/L $KMnO_4$ was prepared by dissolving 1.9868 g $KMnO_4$ in 500 mL of water and then stored in an amber-glass bottle in the dark. 5-SA was obtained from Sigma Chemical Co. (St. Louis, Missouri) and its solutions were used freshly in order to avoid oxidation by dissolved oxygen. All other chemicals were of the highest purity commercially available. De-ionized water was purified with a Milli-Q water ion-exchange system (Millipore Co., USA) for a resistivity of 18 MΩ cm and used throughout the experiment.

2.2. TiO_2 preparation and its surface modification

TiO_2 nanoparticles were synthesized by the hydrolysis and condensation of titanium(IV) n-butoxide in iso-propyl alcohol [27]. *In situ* surface modification was carried out through stirring TiO_2 nanoparticles for 60 min in the solution of 5-SA with different surface modification levels (0, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100% of its saturated adsorptive capacity amount of 5-SA by TiO_2 nanoparticles, *i.e.*, 27.58 μg/mg) at solution pH 2.0. It was worth noting that the color of the TiO_2 surface changed into yellow quickly, implying that a chemical reaction took place (*i.e.*, chemisorption) between 5-SA (surface modifier) and TiO_2. After filtered with 0.22 μm membrane filter, the modified TiO_2 was washed with water for three times and then heat-treated for 30 min at 105 °C. The catalysts prepared in this way were denoted as TiO_2, 10%5-SA_TiO_2, 20%5-SA_TiO_2, 30%5-SA_TiO_2, 40%5-SA_TiO_2, 50%5-SA_TiO_2, 60%5-SA_TiO_2, 70%5-SA_TiO_2, 80%5-SA_TiO_2, 90%5-SA_TiO_2, and 100%5-SA_TiO_2.

2.3. Experimental method

A cylindrical Pyrex photoreactor with a 160 W high-pressure mercury lamp was used, surrounded by a circulating water jacket (Pyrex) to cool the reaction solution. A given amount of photocatalyst, organic pollutants (or KHP), and $KMnO_4$ solution was added to the photoreactor and. The volume of reaction solution was 100 mL for each experiment. The pH of the solution was adjusted with H_2SO_4 (or NaOH) and monitored by a pHB-4 pH meter. The suspension was sampled (4 mL) under magnetically stirring for each given irradiation time interval and centrifuged at 14,000 rpm to remove the photocatalyst particles. The concentration of the obtained MnO_4^- solution was measured at 525 nm by a UV–vis scanning spectrophotometer (Perkin Elmer Lambda 900). All measurements were repeated three times.

3. Results and discussion

3.1. Effect of surface modification degree on the photocatalytic determination of COD

After TiO_2 nanoparticles were *in situ* surface modified by the chemisorption of 5-SA, (a) its UV–vis wavelength response range was expanded from 380 to 600 nm [27]; (b) its band gap was decreased from 3.10 eV to 2.95 eV [27]; (c) its adsorption affinity between the photocatalyst and organic maters was improved by surface function groups of 5-SA_TiO_2, including phenyl, —SO_3H, —COOH, and —OH, so the migration rate for organic maters onto the surface of the photocatalyst were increased; and (d) its photodegradation activity on 4-nitrophenol and dye was improved [10,27]. Therefore, the photocatalytical performance of TiO_2 nanoparticles on refractory organic pollutants and then the photocatalytical determination of COD could be enhanced by *in situ* surface modification of 5-SA.

During photocatalytic oxidation of KHP or organic pollutant, the co-existed $KMnO_4$ was stoichiometrically involved *via* photocatalytic reduction [15]. The COD value is proportional to the depletion of MnO_4^- (ΔC_{Mn}) arising from the photocatalytic reduction of $KMnO_4$ [15]. Here, $\Delta C_{Mn} = C_0 - C_t$, where C_0 and C_t represented the concentrations of MnO_4^- before and after the irradiation, respectively.

The effect of surface modification degree of 5-SA for TiO_2 nanoparticles on photocatalytic determination of COD was illustrated in Fig. 1. When pure TiO_2 was replaced by 5-SA_TiO_2 with surface modification degree from 0% to 40% and 90%, the value of ΔC_{Mn} was increased significantly. For each of given COD values, when 90%5-SA_TiO_2 was used as the photocatalyst, ΔC_{Mn} attained its maximum, which was improved from 0.41 to 0.82 (*i.e.*, 2.0 times) for COD value of 10 mg/L and from 0.21 to 0.44 (*i.e.*, 2.1 times) for COD value of 4 mg/L, respectively.

3.2. Selection of pH value

The photocatalytic performance was greatly affected by the pH value. Some selected samples at different pH values were used to evaluate the effect of pH value on the depletion of MnO_4^- and the results were shown in Fig. 2. Such effect was quite similar between TiO_2 and 90%5-SA TiO_2. With the increasing of pH value from 2.0 to 3.0, the depletion of MnO_4^- was increased slightly but decreased rapidly when pH values were beyond 3.0. Consequently, pH 3.0 was selected for further experiments. This result was similar as surface-fluorinated-TiO_2–$KMnO_4$ photocatalytic system [15]. The adsorption and photodegradation of organic pollutants was closely dependent on pH, achieving a maximum at pH 3.0–5.0 in visible light assisted 5-SA_TiO_2 photocatalytic system [10,27], at the