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Spectroscopic analyses on ROS generation catalyzed by TiO_2, CeO_2/TiO_2 and Fe_2O_3/TiO_2 under ultrasonic and visible-light irradiation

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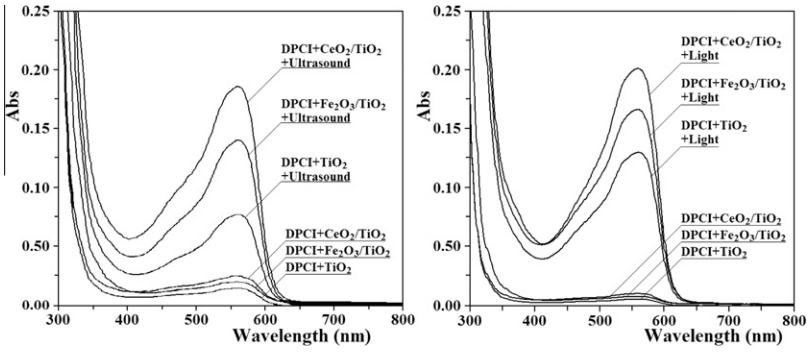
HIGHLIGHTS

- ROS were detected by the method of Oxidation-Extraction Photometry (OEP).
- The formations of ROS were studied during sonocatalytic and photocatalytic process.
- The kinds of ROS were determined by adding some radical scavengers.
- The sonocatalytic and photocatalytic degradation of dyes were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the TiO_2, CeO_2/TiO_2 and Fe_2O_3/TiO_2 powders were irradiated, respectively, by ultrasound and visible-light, and the generation of reactive oxygen species (ROS) were estimated by the method of Oxidation-Extraction Photometry (OEP). That is, the 1,5-diphenyl carbazide (DPCI) can be oxidized by generated ROS into 1,5-diphenyl carbazone (DPCO), which can be extracted by mixed solvent of benzene and carbon tetrachloride. The DPCO extract liquor displays an obvious absorbance at 563 nm wavelength. In addition, some influencing factors, such as (ultrasonic or visible-light) irradiation time, catalyst addition amount and DPCI concentration, on the generation of ROS were also reviewed. The results indicated that the quantities of generated ROS increase with the increase of (ultrasonic or visible-light) irradiation time and catalyst addition amount. Moreover, the displayed quantities of ROS are also related with DPCI concentration. And then, several radical scavengers were used to determine the kinds of the generated ROS. At last, the researches on the sonocatalytic and photocatalytic degradation of several organic dyes have also been performed. It is wished that this paper might offer some important subjects for broadening the applications of sonocatalytic and photocatalytic technologies in future environment treatment.

Introduction

The discharge of organic pollutants in the environment undoubtedly possesses serious health-risks that threatened human survival. Now, more than ever, it is the most important and urgent for human beings to control and treat environmental pollution. Since the beginning of the 21st Century, the application of photocatalytic technology using some semiconductor metal oxides to solve the environmental problems has been received much attention [1–6]. A large number of studies show that the heterogeneous photocatalysis through light illumination on a surface of semiconductor metal oxides is an attractive advanced oxidation process (AOPs) [7–9]. It involves the generation of reactive oxygen species (ROS) like superoxide anion ($\cdot O_2^-$), hydroxyl radical ($\cdot OH$), hydrogen peroxide (H_2O_2) and singlet oxygen ($^1O_2$) and so on [10–12]. These

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oxidizing substances with higher reaction activity than common oxygen molecules can completely destroy various organic pollutants in wastewater [13]. By contrast, as regarding to ultrasonic and visible-light irradiation, the efficiency of photocatalytic degradation is generally higher than that of the sonocatalytic degradation. However, due to the sewage with high concentration or low transparency, as a necessity choice the ultrasound can be applied as an excited source replacing light irradiation. It has been reported that titanium dioxide (TiO_2) or zinc oxide (ZnO) as a sonocatalyst could perform various sonocatalytic reactions when was irradiated by ultrasound. And then, the accompanying sonocatalytic technology has been successfully used in the degradation of organic compounds and dye pollutants [9,14–16]. In addition, some rare earth oxides (for example: CeO_2) have broadly been used in luminous materials, electronic ceramics, polishing powder, and also used as efficient catalyst in photocatalytic field [17–19]. It has been reported that the composite made up of TiO_2 and CeO_2 could bring a special electron transfer process which is able to facilitate the separation of the electron–hole pairs and improve the photocatalytic activity of TiO_2 [17,18]. What is more, Fe_2O_3 as a semiconductor metal oxide has relatively narrow band gap (Eg = 2.2 eV). Hence, the coupling of Fe_2O_3 with TiO_2 causes a wide respondent spectrum, and then improves the utilization of visible light [20–22]. So the CeO_2/TiO_2 and Fe_2O_3/TiO_2 composites were taken as the sonocatalyst and photocatalyst for treating various organic pollutants. Nevertheless, as a new AOPs, the reaction mechanism of sonocatalytic degradation as well as the relevant ROS have not been studied yet in detail. This paper attempts to research how to enhance the sonocatalytic degradation efficiency and search new sonocatalysts. Hence, it is necessary to study the sonocatalytic degradation process and determine the kind of generated ROS.

In recent years, the electron spin resonance, chromatography, chemiluminescent method and some other technologies have been used in the study on the formation and identification of ROS [23–26]. These detecting techniques have high precision, but factually they are limited by some other drawbacks such as the need for expensive laboratory equipment, the complexity of the experiment, heavy detection workload and too many limiting factors. Otherwise, due to the half-life of ROS is very short, and that a series of experiments must dynamically be conducted, it is certainly difficult and inconvenient to directly trace and detect the ROS. The Oxidation-Extraction Photometry (OEP) method has all through been applied to prove the existence of various oxidizing substances through adding 1,5-diphenyl carbazide (DPCI) as capturing reagent [27–29]. The DPCI can be oxidized by oxidizing substances into 1,5-diphenyl carbazone (DPCO), which can be extracted by organic solvents and show an absorbance in a certain range of wavelength. As well known, the ROS has a very strong oxidizability. Therefore, the DPCI should also be oxidized by ROS easily. Because of fast and accurate detection, simple equipment requirements, low-cost reagent, wide detection range and simple requirements for sample, the OEP method could be widely applied in various biological and chemical systems. Theoretically, the quantities and kinds of generated ROS should be evaluated by the amount of oxidized DPCI and the adding of different ROS quencher, respectively. For example, L-Histidine (His) can quench $^1O_2$, 2,6-Di-tert-butyl-methylphenol (BHT) and Dimethylsulfoxide (DMSO) can do ·OH, and that the Vitamin C (VC) is able to quench almost all kinds of ROS. If the absorbance of DPCO obviously decreases after adding some kind of ROS scavenger, it will demonstrate that there is a kind of corresponding ROS existing in the system.

In this work, TiO_2, CeO_2/TiO_2 and Fe_2O_3/TiO_2, taken as the sonocatalyst and photocatalyst, were irradiated by ultrasound and visible-light, and the generated ROS was estimated by the OEP method. In this process, the synergistic effect of TiO_2, CeO_2/TiO_2 or Fe_2O_3/TiO_2 and ultrasonic irradiation or visible-light irradiation was evaluated during the generation of ROS. In addition, the effect of some influencing factors, such as (ultrasonic and visible-light) irradiation time and TiO_2, CeO_2/TiO_2 or Fe_2O_3/TiO_2 addition amount on the generation of ROS were reviewed. The effect of DPCI concentrations on the generated quantities of ROS was also considered. Meanwhile, several ROS quenchers were used to determine the kinds of generated ROS. At last, referring to corresponding reports [30–33], the sonocatalytic or photocatalytic degradation of some organic dyes in aqueous solutions, that is, under ultrasonic or visible-light irradiation combined with TiO_2, CeO_2/TiO_2 and Fe_2O_3/TiO_2 were studied. It is wished that this paper might offer some important references for broadening the applications of sonocatalytic and photocatalytic technologies and developing new efficient catalysts in future environment treatment.

Experimental

Materials

The nano-sized CeO_2, Fe_2O_3 and TiO_2 (anatase phase) powders (Veking Company, China) were used for preparing the CeO_2/TiO_2 and Fe_2O_3/TiO_2 composites. Malachite Green, Acid Red B, Methylene Blue, Congo Red and Azo Fuchsine (AR grade, Tianjin Kaiyuan Reagent Corporation, China) were used as model organic pollutants for evaluating the catalytic activity of TiO_2, CeO_2/TiO_2 and Fe_2O_3/TiO_2 composites. Their molecular structures were given in Fig. 1. 1,5-diphenyl carbazide (DPCI), L-Histidine (His), 2,6-Di-tert-butyl-methylphenol (BHT), Dimethylsulfoxide (DMSO) and Vitamin C (VC) (purity > 99.0%, Sinopharm Chemical Reagent Co., Ltd., China) were used to determine the amount and kind of the generated ROS. Benzene and carbon tetrachloride (AR grade, Shenyang Dongxing Reagent Factory, China) were used as extracting agent. The other chemical reagents were all of analytical reagent grade, and double distilled water was used for solution preparation.

Apparatus

The experimental setups are shown in Fig. 2. The Controllable Serial-Ultrasonics apparatus (SG3200HE, Shanghai GuTel Ultrasonic Instrument Company, China) operating at ultrasonic frequency of 40 kHz, output power of 50 W and irradiation intensity of 1.0 W/cm^2 through manual adjusting and visible-light irradiation apparatus (EFD18D/65-E3U, Toshiba Company, Japan) operating at visible-light emitting diodes of 50 Hz power supply

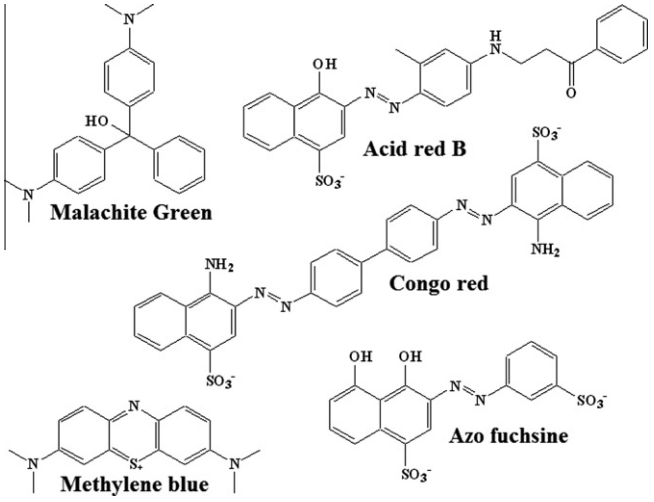

Fig. 1. Molecular structures of Malachite Green, Acid Red B, Methylene Blue, Congo Red and Azo Fuchsine.