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Assisted sonocatalytic degradation of pethidine hydrochloride (dolantin) with some inorganic oxidants caused by CdS-coated ZrO_2 composite

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ABSTRACT

CdS was synthesized via hydrothermal method and CdS-coated ZrO_2 composite was prepared via chemical precipitation method. And then they were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). After that, the sonocatalytic degradation of pethidine hydrochloride (dolantin) in aqueous solution was conducted adopting CdS-coated ZrO_2 composite as sonocatalyst with inorganic oxidant assisted. In addition, some influencing factors such as inorganic oxidant kind, including persulfate ($K_2S_2O_8$), perchlorate ($NaClO_4$) and periodate (KIO_4), inorganic oxidant concentration and ultrasonic irradiation time on sonocatalytic degradation of pethidine hydrochloride were examined by using gas chromatograph. The experimental results showed that the used inorganic oxidants can effectively assisted the sonocatalytic degradation of pethidine hydrochloride caused by CdS-coated ZrO_2 composite and the increase effects arrange as the order of $K_2S_2O_8$ > KIO_4 > $NaClO_4$. And the best sonocatalytic degradation ratio (95.50%) of pethidine hydrochloride could be obtained when the conditions of 10.00 mmol/L $K_2S_2O_8$, 1.00 g/L prepared CdS-coated ZrO_2 composite, 135 min ultrasonic irradiation (40 kHz frequency and 300 W output power), 100 mL total volume and 25–28 °C temperature were adopted. However, only using CdS-coated ZrO_2 as sonocatalyst without any inorganic oxidants merely reaches 20% degradation ratio of pethidine hydrochloride when other conditions are the same. The method of sonocatalytic degradation assisted with inorganic oxidants may be an efficient sonocatalytic system for degradation of pethidine hydrochloride.

1. Introduction

Narcotic drugs abuse may do harm to people's health by making person produce the physical and mental dependence [1]. What is worse, it makes families into economic bankruptcy even leads to the harrowing break-up. Pethidine hydrochloride (dolantin) is a phenylpiperidine derivative, which is firstly synthetic analgesic drug to achieve the wide therapeutic use [2,3]. Acting as an opiate agonist, pethidine hydrochloride has the similar pharmacological effect with morphine [4]. Long-term abuse and accidental ingestion will result in dependence and damage of central nervous system (CNS), even lead to death [5,6]. On a global scale, many pharmaceutical factories in the production of pethidine hydrochloride would discharge waste water containing pethidine hydrochloride into our environment [7]. On the other hand, every year some hospitals would also produce a lot of out-of-date pethidine hydrochloride. What's more, public security organ could seize a large number of pethidine hydrochloride every year. So the harmless treatment of pethidine hydrochloride is a major problem that we must face to. In the past, there were some methods to dispose pethidine hydrochloride, such as incineration, landfill, adsorption and so on [8]. Nevertheless, these methods are generally incomplete and insecure, even often bring secondary pollution. Therefore, it is indispensable to seek a better way to dispose pethidine hydrochloride. Perhaps, for a special biological active substance breaking its molecular structure and chemical composition to reach the harmlessness may be feasible.

The sonocatalytic technology combining with semiconductors has been received much attention in solving environmental problems [9–12]. Because of many advantages, such as strong

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penetrability, special transmission mode, high efficiency and simple operation, therefore, it can become an effective way to decompose the organic dyes in non- or low-transparent effluents [13–15]. Perhaps, this way should also be feasible to dispose narcotic drugs. In the past, sonocatalytic degradation of many organic pollutants employing titanium dioxide (TiO_2) powder as sonocatalyst has been reported [16–19]. The bandwidth of TiO_2 is 3.2 eV, and its valence band (VB) and conduction band (VB) electric potentials are 2.91 eV and −0.29 eV [20], respectively. For most of organic pollutants, TiO_2 is enough to effectively decompose them through photocatalytic or sonocatalytic reaction process [21,22]. Nevertheless, narcotic drugs are some stable substances chemically. Apparently, in order to destroy narcotic drugs, it is necessary to select some of broadband semiconductor oxides as sonocatalysts. Due to the bandwidth of 5.0 eV and relatively low VB electric potential of 3.91 eV, ZrO_2 should have much stronger oxidation capacity under ultrasonic irradiation [23–25]. However, because of such wide bandwidth of ZrO_2, only a small portion of ultraviolet light in sonoluminescence can be used [26–28]. In order to broaden the response range towards light and avoid the recombination of electron (e^-)-hole (h^+) pairs, using a narrowband semiconductor to combine with ZrO_2 may be feasible [29–33]. CdS has bandwidth of 2.42 eV and is an applicable semiconductor. Being similar to photocatalytic reaction, such combination will enhance the sonocatalytic activity of ZrO_2 [34–37].

In this paper, the nano-sized CdS was synthesized via hydrothermal method and the CdS-coated ZrO_2 composite was prepared via chemical precipitation method. And then the CdS-coated ZrO_2 composite was chosen as sonocatalyst to carry out sonocatalytic degradation of pethidine hydrochloride. In addition, it has been reported that the addition of inorganic oxidants could further enhance the sonocatalytic degradation efficiency of pollutants [38–41]. Therefore, in this study, some inorganic oxidants were used to assist sonocatalytic degradation. Through the reaction of inorganic oxidants with the electrons on the conduction band (CB) of ZrO_2, the reactive oxygen species (ROS) oxidants can be generated. The influences of inorganic oxidant kind and concentration as well as ultrasonic irradiation time on the sonocatalytic degradation of pethidine hydrochloride were studied. The degradation process and corresponding mechanism were tentatively proposed. It is wished that the sonocatalytic degradation method assisted with inorganic oxidants can be used to treat the narcotic drugs in aqueous solution.

2. Experimental

2.1. Materials and reagents

Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$) and sodium sulphide nonahydrate ($Na_2S{\cdot}9H_2O$) (Sinopharm Chemical Regent Co, Ltd., China) were used to prepare the nano-sized cadmium sulphide (CdS). Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) and ammonium hydroxide (Sinopharm Chemical Regent Co, Ltd., China) were used to prepare the nano-sized ZrO_2. Pethidine hydrochloride (99.99% purity, Tianjin Kaiyuan Reagent Corporation, China) was used to undergo the sonocatalytic degradation. Potassium persulfate ($K_2S_2O_8$), sodium perchlorate ($NaClO_4{\cdot}H_2O$) and potassium periodate (KIO_4) (AR, Tianjin Kemiou chemicals Corporation, China) were purchased as assisted inorganic oxidants. Lidocaine (Sigma-Aldrich, MO, USA) was used as internal standard. All the reagents were of analytical purity grade, and were directly used without further purification.

X-ray powder diffractometer (XRD, D-8, Bruker-axs, Germany, Ni filtered Cu Ka radiation in the range of 2θ from 10° to 70°), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan) and scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan) were used to determine the crystalline phase. X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo, America) was used to determine the element type and composition content of CdS-coated ZrO_2 composite. Gas chromatograph Agilent 6890 (Agilent technologies, Massy, France) was used to inspect the sonocatalytic degradation ratio of pethidine hydrochloride in aqueous solution. Controllable Serial-Ultrasonics apparatus (KQ-300, Kunshan Company, China) was adopted to irradiate the pethidine hydrochloride aqueous solution, operating at ultrasonic frequency of 40 kHz and output power of 300 W through manual adjust. Apparatus of ultrasonic irradiation has been shown in our past work [42,43].

2.2. Preparation of nano-sized CdS powder

Nano-sized CdS particles were prepared by using a hydrothermal method. 6.0 mmol of $CdCl_2{\cdot}2.5H_2O$ was dissolved in 40 mL distilled water, then 6.0 mmol sodium sulphide Na_2S solution was added with continuous stirring for 30 min. Subsequently, the solution was transferred into a 50 mL polytetrafluoroethylene (PTFE) autoclave equipped with a stainless steel shell and maintained at 100 °C for 4.0 h. After cooling to room temperature, the orange precipitation was collected through filter and washed several times alternately with ethanol and distilled water, and then vacuum-dried at 80 °C 3.0 h followed by calcination in air for 3.0 h at 500 °C and grinded for the following experiments and characterizations.

2.3. Preparation of sonocatalysts CdS-coated ZrO_2 composite

ZrO_2 prepared by chemical precipitation method [44]. 5.80 mmol (1.8691 g) of zirconium oxychloride $ZrOCl_2{\cdot}8H_2O$ was dissolved in 50 mL of deionised water and precipitated the hydroxides with an aqueous solution of 6.0% NH_3 at pH 9.9 and stirred vigorously. The precipitate was filtered and washed to make it free from chloride ion and ammonia, and then dissolved in a small amount of water. After that 1.90 mmol (0.2810) g of nano-sized CdS powder was added to the above solution with stirring vigorously. Then filtered and washed with distilled water. The washed product was dried at 120 °C in air for 12 h followed by calcination in air for 3.0 h at 350 °C. After fully grinding, the CdS-coated ZrO_2 composite was obtained.

2.4. Characterization of the prepared CdS-coated ZrO_2 composite

The prepared CdS-coated ZrO_2 composite particles as sonocatalysts were characterized by X-ray powder diffractometer (XRD, D-8, Bruker-axs, Germany, Ni filtered Cu Kα radiation in the range of 2θ from 10° to 70°), scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan) and X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo, America).

2.5. Measurements of sonocatalytic activity of the prepared CdS-coated ZrO_2 composite

Sonocatalytic degradation experiments of pethidine hydrochloride were carried out in a 150 mL erlenmeyer flask placed in an ultrasonic irradiation apparatus (300 (length) × 180 mm (width) × 120 mm (height), KQ-300, 40 kHz, 300 W, six transducers, Kunshan ultrasonic apparatus Company, China) under air atmosphere. In the common experiment, 1.00 g/L CdS-coated ZrO_2 composite, 2.70 g/L (10.00 mmol/L) $K_2S_2O_8$, 2.30 g/L (10.00 mmol/L) KIO_4, 1.23 g/L (10.00 mmol/L) $NaClO_4$ and 10.00 mg/L pethidine hydrochloride concentration in 100 mL total volume were adopted to perform the sonocatalytic degradation. Before ultrasonic irradiation, the