

Synthesis of novel sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ and its application for sonocatalytic degradation of methamphetamine hydrochloride



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ARTICLE INFO

Keywords:

Up-conversion luminescence agent
($\text{Er}^{3+}:\text{YAlO}_3$)
 $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composite sonocatalyst
Methamphetamine hydrochloride
Sonocatalytic degradation

ABSTRACT

The composited sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was prepared by ultrasonic dispersion and high temperature calcinations method. The microstructure of $\text{Er}^{3+}:\text{YAlO}_3$ was prepared via sol-gel method and Nb_2O_5 was prepared by hydrothermal method. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX), ultraviolet–visible (UV–vis) spectra and photoluminescence (PL) spectra, respectively. The sonocatalytic decomposition activity of composite sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was investigated by using ultrasound as sound source and methamphetamine hydrochloride as the target degradation product. The influences of composite sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ with different ratios, calcination temperature, ultrasonic power, ultrasonic temperature and recycle times were investigated. The results showed that the sonocatalytic degradation rate was 82.17% after 5 h sonocatalytic decomposition under the condition of ultrasonic power of 700 W, frequency of 45 kHz and surrounding temperature of 30 °C. The sonocatalytic degradation ability of composite sonocatalyst for methamphetamine hydrochloride in aqueous solution was still good after recycled five times. The hydroxyl radicals ($\cdot\text{OH}$) and holes (h^+) are identified and hydroxyl radicals ($\cdot\text{OH}$) plays a major role during the oxidation process. The experimental results show that sonocatalytic is a new idea for the harmless treatment of amphetamine-type stimulants.

1. Introduction

It is estimated that 250 million people between the ages of 15 and 64 years used at least one drug including methamphetamine, which over 27 million people are drug abusers in the year 2014 according to World Drug Report 2016. The global market for synthetic drugs is continuously to be dominated by methamphetamine. The increasingly diversified drug market is expanding in East and South-East Asia, where it accounts for a large share of the people receiving treatment for drug use in a number of countries, and use of methamphetamine is increasing in parts of North America and Europe [1]. Methamphetamine molecular formula: $\text{C}_{10}\text{H}_{15}\text{N}$, its base is a colorless volatile oil insoluble in water, ammonia smell, boiling point 214 °C, soluble in ethanol, ethyl acetate and other organic solvents and slightly soluble in water. It has a melting point range from 172 °C to 174 °C, soluble in methanol and water, soluble in weak polar organic solvent. Methamphetamine hydrochloride is a colorless crystal by reaction of methamphetamine and hydrochloric acid. It is described as “ice, crystal meth or crystal methamphetamine” due to its form and appearance.

As a kind of synthetic central nervous system stimulant,

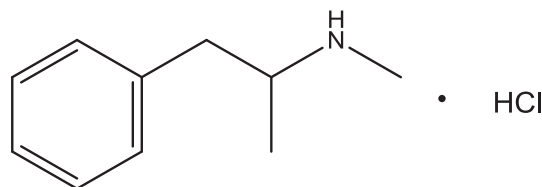
Methamphetamine hydrochloride could affect the euphoria center of brain and appear the central excited effect. Meanwhile, it could also stimulate the medulla oblongata respiratory system, excite the cardiovascular system, causing increased blood pressure, accelerated heart rate and raised body temperature. Moreover, methamphetamine hydrochloride could inhibit the feeding center and leading to loss of appetite. Overdose abuses could appear some psychiatric symptoms such as hallucinations, delusions and paranoid schizophrenia as well as cognitive dysfunction. Long-term crystal meth abuse could lead to permanent damage of nervous system, and even life threatening.

Methamphetamine hydrochloride has a more stable chemical property. Crystal methamphetamine is a form of the drug that looks like glass fragments or shiny, bluish-white rocks, which is convenient to store, transport and use. Nowadays, international drug market is flooded with ice and forms of pills with the main ingredients of crystal ice called “magu”. A wide range of crystal meth abuse to the society has brought serious social problems [2–5]. According to Annual Report on Drug Control in China 2016, crystal meth abuse was the most serious type that 531,000 new drug abusers were detected and crystal meth abusers accounted for 73.2% in 2015. There were 336 extreme cases of

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violent attacks, suicide, self mutilation and drugged driving accident caused by drug abuse. 144 tons of Ice and amphetamine type drugs were seized all over the world in 2014. China busted 484 cases related to crystal meth, seized 36.6 tons of crystal meth in 2015 [6]. Besides that, Wastewater and solution produced in the process of the formation of methamphetamine hydrochloride contaminated river, lake, waters by tons of calculation. To destroy such huge amounts of methamphetamine and its liquid, we face enormous pressure and challenge. Drugs are usually destroyed by means of incineration, landfill and sea abandon through the world [7–10]. However, such methods cannot be totally solved for large amounts of methamphetamine hydrochloride aqueous solutions, and inevitably exhibited many disadvantages or limitations [11,12], and even caused damage to the environment, gradually restricted and criticized by relevant laws and environmentalists [13,14]. So it is a critical challenge for governments to explore scientific, effective and harmless ways to solve such problems. In view of the particularity of narcotic drugs, some methods such as Advanced Oxidation Processes (AOPs) may be feasible [15–19].

In recent years, the semiconductor sonocatalytic technology in the field of organic degradation has made considerable progress, which has brought new ideas for the harmless treatment of methamphetamine hydrochloride. In the past, most researchers applied TiO_2 sonocatalytic method to degrade organic pollutants [20–24]. However, some semiconductor materials have wider band gap and higher oxidation potential compared with TiO_2 sonocatalysts [25–29]. A large number of studies have shown that the efficiency of photocatalytic oxygen evolution by some of perovskite niobate is one order higher than that by TiO_2 sonocatalyst [30,31]. Nb_2O_5 is an important inorganic semiconductor material, its excellent catalytic performance has aroused widespread concern in recent years [32–34]. Nb_2O_5 is an important n-type wide bandgap semiconductor material, the band gap was 3.4 eV in room temperature, the melting point was 1460 °C, and the semiconductor was insoluble in water [35]. The catalyst was dissolved in concentrated sulfuric acid and hydrofluoric acid, insoluble in other acids [36]. Thus, Nb_2O_5 sonocatalytic has high stability in water solution. Nb_2O_5 has three crystal phases at different temperature, such as typically hexagonal (H- Nb_2O_5), orthorhombic (O- Nb_2O_5), and monoclinic (M- Nb_2O_5). Among these crystalline forms, the most thermodynamically unstable form was H- Nb_2O_5 , and the most stable form was M- Nb_2O_5 . The transition temperature that the hexagonal crystal phase translated into orthorhombic crystal phase was 500–800 °C, and the temperature of the continued transition to the monoclinic phase was 1000 °C or more [37]. It is reported that the hexagonal Nb_2O_5 has high sonocatalytic activity, and the nanorods with one-dimensional structure were more active than nanospheres for the degradation of methylene blue [38]. Considering that we commonly seized a large number of methamphetamine hydrochloride liquids which contain dark light-proof hydrochloric acids in a clandestine plant, we give up traditional photocatalytic degradation and turn to well penetrating sonocatalytic degradation study. Due to some semiconductor materials can only absorb short wavelength sonoluminescence, we added up-conversion luminescence agent to make long wavelength into short wavelength to enhance the degradation efficiency for semiconductor material [39]. In recent years, we have done some work on the use of the up-conversion luminescence agent to improve the catalytic degradation activity of the sonocatalyst [40]. In this work, we have designed a composite material $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$, the up-conversion luminescence agent of $\text{Er}^{3+}:\text{YAlO}_3$ combined with nanometer Nb_2O_5 , to perform sonocatalytic degradation of methamphetamine hydrochloride. At the same time, the main influence factors on the ultrasonic degradation activity were investigated. In addition, the mechanism for sonocatalytic degradation of methamphetamine hydrochloride is also proposed. We mixed the seized crystal meth in aqueous solution by such method, added moderate composite catalysts to degrade in the condition of ultrasound. The method also applied to different colors and concentration of waste water treatment, which contain methamphetamine hydrochloride



Scheme 1. The structure of the methamphetamine hydrochloride.

seized from clandestine laboratory. The method is simple, rapid, efficient, green and non-toxic, which provides new techniques and ideas for drug degradation in the field of drug control. It also provides great theoretical and practical significance.

2. Experimental

2.1. Materials and reagents

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and HNO_3 were purchased from Sinopharm Shenyang Chemical Reagent Co., Ltd. $\text{C}_2\text{H}_5\text{OH}$, HF, CH_3COOH and citric acid were purchased from Beijing Chemical Reagent Co., Ltd. All above chemical reagents were analytical grade. Er_2O_3 , Y_2O_3 , and citric acid were purchased from Aldrich reagent of America, and the purity was 99.99%. Methamphetamine hydrochloride (as shown in Scheme 1) was purchased from the National Drug Standard Laboratory of China with a purity of 99%. All experimental water was double-distilled water.

The morphology and dispersion of the sonocatalytic degradation materials were characterized by X-ray powder diffractometer (D-8, Bruker-axs, Germany, Ni filtered Cu K α radiation in the range of 2 θ from 10° to 70°), scanning electron microscopy (JSM-6510LV, Nippon Electronics Co., Ltd.). Energy dispersive X-ray analysis (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan) was used to determine the element types and composition. To examine optical absorption properties of the prepared samples, ultraviolet–visible (UV–vis) spectra of the samples were measured on a Shimadzu UV-3600 spectrometer using BaSO_4 as a reflectance standard. The photoluminescence (PL) spectra were acquired by using a fluorescence spectrophotometer (Hitachi High-Tech F-7000) at the excitation wavelength of 448 nm and 657 nm. The sonocatalytic degradation rate was measured by gas chromatograph (7890B, Agilent, USA) and 7 gas chromatography mass spectrometry (890A-5975C, Agilent, USA). Centrifuge (TDL80-2B, Zhangjiagang City Light Industry Equipment Factory) was used for high-speed centrifugal treatment of the sample after sonocatalytic degradation. Desktop three-frequency constant temperature CNC ultrasonic cleaner (KQ-700GVDV, Kunshan City ultrasound Instrument Co., Ltd.) was used as sound source on the sonocatalytic degradation process. Tube furnace and muffle furnace (Baixin industrial furnace company of Shenyang), magnetic heating stirrer (Jintan Jiangnan Co., Ltd.), FA2004 analytical balance (Germany Sartorius) and 101-1 type electric blast drying box (Shanghai Xinnuo Instrument Factory) were used for synthesis of sonocatalyst.

2.2. Preparation of nano-sized Nb_2O_5 powder

0.40 g Nb_2O_5 and 10 mL 40% hydrofluoric acid (HF) were transferred into Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h, obtained colorless transparent NbF_5 . Then, added 25%–28% ammonia to the whole precipitation, filtration, and washed with water several times until the fresh niobic acid was obtained. Subsequently, 0.3 g of niobate was washed with deionized water and placed in a Teflon-lined stainless steel autoclave volume of 25 mL and 10 mL of glacial acetic acid and 0.5–0.6 g ammonium oxalate were added to the Teflon-lined stainless steel autoclave. The reactants were sealed in the oven at 160–180 °C in constant temperature for heating 24–26 h. Then,

the reaction tank had cooled down to room temperature, filtration products and ethanol and deionized water were used for cleaning 3–4 times. After drying at 50 °C, Nb₂O₅ nanopowder was obtained, and the resulting sample was calcined at 400 °C for 1 h in a tube furnace to obtain Nb₂O₅ nanoparticles [37].

2.3. Preparation of sonocatalysts Er³⁺:YAlO₃ composite

Er³⁺:YAlO₃ nanocrystals were synthesized by sol-gel method, in which citric acid (99.99%) was used as chelating agent [41]. 0.0464 g Er₂O₃ and 2.7281 g Y₂O₃ were dissolved respectively in concentrated nitric acid and heated by stirring into colorless and transparent form. In another beaker, 9.0633 g Al(NO₃)₃·9H₂O dissolved in distilled water slowly added to the above rare earth ion solution, while stirring by a glass rod at room temperature. Subsequently, 30.4649 g of citric acid dissolved in distilled water as a chelating agent and cosolvent, then added to the above solution. Finally, foamy viscous solution was obtained by heating and stirring at 50–60 °C for a period. The viscous solution was placed into the oven at a constant temperature of 80 °C by heating for 36 h, foam sol was obtained. The resulting sol was heated at 500 °C for 50 min, and then calcined at 1100 °C for 2 h. Finally, the sintered material was removed from the high temperature furnace and cooled down to room temperature in air to obtain Er³⁺:YAlO₃ powder.

2.4. Prepared of Er³⁺:YAlO₃/Nb₂O₅ composite

According to previous research results, ultrasonic assisted preparation has the advantage of uniformity of the reaction, making the prepared synthetic materials more suitable for sonocatalytic reaction [42]. Nb₂O₅ nanopowder and the appropriate amount of Er³⁺:YAlO₃ well grinded in an agate mortar. Then, the mixtures were transferred into the 100 mL beaker and continued to add 10 mL of anhydrous ethanol and 20 mL of water. The beaker was sealed with plastic film for 30 min ultrasonic dispersion, warmed up from room temperature to 30 °C, after which was removed in magnetic stirrer until it became dry via stirring and heating. The mixed powders were well ground with an agate mortar into 5 copies, which were placed respectively into the crucible, heated at a rate of 20 °C/min in the muffle furnace until the temperature reached at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C then kept for 1 h. YAlO₃/Nb₂O₅ composites were obtained.

2.5. The experiments for sonocatalytic decomposition of methamphetamine hydrochloride

50 mg of Er³⁺:YAlO₃/Nb₂O₅ composite was accurately weighed into a 250 mL stoppered flask equipped with 50 mL of 10 mg/L of a simulated aqueous solution of methamphetamine hydrochloride. The mixed solutions were allowed to mix well and fully adsorbed without using ultrasonic. Subsequently, the conical flask was placed in a constant temperature CNC ultrasonic cleaner and subjected to a degradation test. The samples were taken every 1 h, and the content of methamphetamine hydrochloride in the sample was measured by a gas chromatograph. The degradation rate was calculated according to the following formula.

$$\text{Degradation ratio (\%)} = (C_0 - C_t) / C_0 \times 100$$

where C₀ was the concentration of undegraded methamphetamine hydrochloride solution, and C_t was the concentration of methamphetamine hydrochloride solution that has been degraded for a certain period of time. In addition, the degradation products were analyzed by means of GC/MS.

Gas chromatographic conditions: Agilent 7890 gas chromatograph equipped with nitrogen and phosphorus detector (NPD). The column was Agilent 19091 J-413 HP-5 fused silica capillary column 30 m × 320 mm (i.d.) × 0.25 μm (film thickness). The temperature was raised from 80 °C to 140 °C at the speed of 10 °C/min by means of the

program warming way and then raised to 280 °C (for 1 min) at a rate of 20 °C/min. The temperature of the detector was 280 °C, the inlet temperature was 250 °C, the carrier gas was N₂, the flow rate was 2 mL/min, the H₂ flow rate was 3 mL/min, the air flow rate was 60 mL/min, and the tail blow flow was 10 mL/min. The injection was carried out by using a splitless pattern. The N, N-dimethylaniline was used as internal standard to quantitatively analyze the solution of methamphetamine hydrochloride by internal standard method.

GC/MS conditions: The chromatographic column was HP-5MS (30 m × 0.32 mm × 0.25 μm) capillary column with high purity helium as a carrier gas. The flow rate of carrier gas was 1.0 mL/min, and the inlet temperature was 280 °C. The column temperature was maintained at 60 °C for 1 min, then increased to 140 °C at a rate of 10 °C/min, and then increased to 280 °C at a rate of 20 °C/min. Transmission line temperature was 250 °C. Electron impact ionization source was used. Electron energy was 70 eV and ion source temperature was 230 °C with splitless injection.

3. Results and discussion

3.1. XRD patterns of the prepared Er³⁺:YAlO₃/Nb₂O₅ composite

Fig. 1-a showed the XRD patterns of the prepared Nb₂O₅ powder, Er³⁺:YAlO₃ powder, and Er³⁺:YAlO₃/Nb₂O₅ composite powder. It can be seen from Fig. 1-a-1 that the characteristic peaks of Nb₂O₅ at 2θ = 22.71°, 28.63°, 36.78°, 46.31°, 50.85° and 55.28°, which were very close to the pure Nb₂O₅ standard card JCPDS # 28-0317 [43]. From Fig. 1-a-1, the characteristic diffraction peaks of Er³⁺:YAlO₃ at 2θ = 24.01°, 34.30°, 41.87°, 42.70°, 49.48° and 61.80° at high temperature treatment of 1100 °C, and were very similar to pure Er³⁺:YAlO₃ standard card JCPDS # 33-0040 [44]. The characteristic diffraction peaks of Nb₂O₅ 2θ = 22.30°, 41.87°, 42.70°, 49.48° and 61.80°, and the Er³⁺:YAlO₃ characteristic peaks at 2θ = 22.71°, 28.63° and 46.31°, which were obvious shown in the Fig. 1-a-3. The results indicated that Nb₂O₅ and Er³⁺:YAlO₃ have been combined into Er³⁺:YAlO₃/Nb₂O₅ complex.

Fig. 1-b showed the XRD patterns of the powders with different mass ratios of Er³⁺:YAlO₃/Nb₂O₅. It can be seen that with the increasing of Er³⁺:YAlO₃ ratio, the characteristic diffraction peak was also increased. Fig. 1-c showed the XRD patterns of Er³⁺:YAlO₃/Nb₂O₅ complex powders at different treatment temperatures. It can be seen that the characteristic diffraction peaks of Er³⁺:YAlO₃/Nb₂O₅ became high and sharp as the calcination temperature increased, indicating that the increase of temperature was favorable for the formation of Er³⁺:YAlO₃/Nb₂O₅ crystals.

3.2. SEM images of the prepared Er³⁺:YAlO₃/Nb₂O₅ composite

Fig. 2 showed the SEM of Nb₂O₅, Er³⁺:YAlO₃ and Er³⁺:YAlO₃/Nb₂O₅ complex powders. From Fig. 2-a, a large number of Nb₂O₅ particles with an average particle size close to 50 nm can be seen, some of which were rod-like. Fig. 2-b showed Er³⁺:YAlO₃, whose particle size was about 300 nm and was ellipsoidal. As can be seen from Fig. 2-c, a large number of particles with a diameter of about 50 nm were uniformly attached to the larger particles around 300 nm in diameter, indicating that Nb₂O₅ and Er³⁺:YAlO₃ had been compounded together.

3.3. EDX spectra of the prepared Er³⁺:YAlO₃/Nb₂O₅ composite

The EDX of Nb₂O₅, Er³⁺:YAlO₃ and Er³⁺:YAlO₃/Nb₂O₅ complex powders were shown in Fig. 3. From Fig. 3-a, there were two strong peaks, namely, Nb, O, and Nb₂O₅, respectively, and the ratio of the two elements was 27.52% and 72.48%, respectively, which was close to the theoretical value. The peaks of O, Er, Al and Y can be seen from Fig. 3-b, indicating that the material consists of four elements, and the ratio of four elements was consistent with the theoretical value of Er³⁺:YAlO₃.

Fig. 1. XRD patterns of (a) the prepared samples (a-1: Nb_2O_5 powder (heat treatment temperature 500 °C, heat treatment time 1 h), a-2: $\text{Er}^{3+}:\text{YAlO}_3$ powder (heat treatment temperature 1100 °C, heat treatment time 2 h), a-3: $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ complex powder (the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.15:1, heat treatment temperature was 500 °C, heat treatment time 1 h), (b) 0.0:1.0–0.3:1.0 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratios in $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (heat-treated at 400 °C for 60 min) and (c) different treatment temperatures $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composite (heat treatment temperatures 400 °C, 500 °C and 600 °C, mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.15:1, heat treatment time was 1 h).

Fig. 3-c contained the peaks of O, Er, Al, Y and Nb and the ratio of these five elements were consistent with the ratio of each element in $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ complex.

3.4. Ultraviolet visible absorption spectra and photoluminescence spectra of Nb_2O_5 , $\text{Er}^{3+}:\text{YAlO}_3$ and $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$

In order to explain the effect of $\text{Er}^{3+}:\text{YAlO}_3$ on the photocatalytic activity of Nb_2O_5 , the UV–visible absorption spectra and photoluminescence spectra of Nb_2O_5 , $\text{Er}^{3+}:\text{YAlO}_3$, $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ were measured. As shown in Fig. 4a, $\text{Er}^{3+}:\text{YAlO}_3$ has an obvious absorption peak in the visible region of 400–800 nm, while Nb_2O_5 does not show that $\text{Er}^{3+}:\text{YAlO}_3$ can absorb visible light. We selected 448 nm and 657 nm as the excitation wavelength for photoluminescence test, the results in Fig. 4b and c, can be 200–400 nm interval to find $\text{Er}^{3+}:\text{YAlO}_3$ emission peak. While Nb_2O_5 got no emission peak in the 200–400 nm interval. In summary, $\text{Er}^{3+}:\text{YAlO}_3$ can absorb long wavelength of visible light into short-wavelength ultraviolet light, and the resulting ultraviolet light can effectively excite Nb_2O_5 , so that it can take photocatalytic reaction in long wavelength light. The Nb_2O_5 with addition of $\text{Er}^{3+}:\text{YAlO}_3$ improves the utilization of light and thus exhibits a stronger photocatalytic activity.

3.5. Effect of different mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 on the ultrasonic degradation of methamphetamine hydrochloride and its reaction kinetics

50 mL of 10 mg/L solution of methamphetamine hydrochloride was

placed in a 250 mL Erlenmeyer flask and 50 mg of heat-treated different mass ratios of catalyst powders at 500 °C for 1 h was added and subjected to ultrasonic degradation. The test was carried out every 1 h for determination methamphetamine hydrochloride degradation rate. Fig. 5a was the sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ combined with different mass ratio, and the degradation rate of the degradation methamphetamine hydrochloride aqueous solution 5 h was calculated. ‘0:0’ curve indicated a blank experiment without adding any catalyst, the degradation rate was 7.39% after 5 h. It can be seen from the above figures that the degradation rate increased with the pass of the degradation time, and obviously increased by the addition of $\text{Er}^{3+}:\text{YAlO}_3$. It was shown that the upconversion agent $\text{Er}^{3+}:\text{YAlO}_3$ was possible to absorb low energy photons and then excited high energy photons, and increased the utilization rate of Nb_2O_5 to sonoluminescence. When the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.15:1, the photocatalytic degradation rate was the highest, and the degradation rate of methamphetamine hydrochloride reached 82.17% after 5 h. In addition, continued to increase the amount of $\text{Er}^{3+}:\text{YAlO}_3$, Nb_2O_5 ratio naturally became smaller, the ability to catalyze the degradation of methamphetamine hydrochloride would also decline. The results showed that the degradation rate of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was reduced to 47.74% when the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.3:1, which indicated that the best degradation effect can only be obtained when the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was appropriate.

In order to further compare the degradation rate of methamphetamine hydrochloride with different mass ratio of composite sonocatalyst, the first order reaction kinetics was established. Fig. 5b shows the curve of $\ln(C_t/C_0)$ versus ultrasonic irradiation time. Where C_t was the

Fig. 2. SEM images of the prepared (a) Nb_2O_5 powder (heat treatment temperature 500 °C, heat treatment time 1 h), (b) $\text{Er}^{3+}:\text{YAlO}_3$ powder (heat treatment temperature 1100 °C, heat treatment time 2 h) and (c) $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ complex powder (the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.15:1, heat treatment temperature was 500 °C, heat treatment time 1 h).

instantaneous concentration, and C_0 was the original concentration. It can be seen from the figure that the four curves approximate a linear relationship, indicating that these sonocatalytic degradation reaction was basically followed by the first order reaction kinetics [$\ln(C_t/C_0) = -kt$], the rate constant was K . The kinetic constants and correlation coefficients of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0:0, 0:1, 0.15:1 and 0.3:1 four proportions) were 0.017 h^{-1} ($R^2 = 0.9543$), 0.0878 h^{-1} ($R^2 = 0.9589$), 0.3484 h^{-1} ($R^2 = 0.9959$), 0.1183 h^{-1} ($R^2 = 0.9411$), respectively. The order of the reaction rate constant was $0.15:1 > 0.3:1 > 0:1 > 0:0$.

3.6. Effect of different calcination temperature on sonocatalytic degradation rate of methamphetamine hydrochloride

Five copies of sonocatalysts $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1) were put into muffle furnaces respectively. The heat-treated temperatures were 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, and each heating time was 60 min, and the heating temperature was slowly heated in the furnace. The solution of the methamphetamine hydrochloride solution was subjected to ultrasonic degradation by using the treated sonocatalyst, and the degradation rate of methamphetamine hydrochloride was measured every 1 h. Fig. 6 was the effect of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1) calcinated at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C for 60 min on the degradation rate of methamphetamine hydrochloride. As was shown from the figure, with the extension of degradation time, the degradation rate increased significantly, while the catalyst activity decreased 5 h later. The degradation efficiency of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ under the

condition of heating at 500 °C was the best. At 500 °C, Nb_2O_5 was hexagonal system. The temperature was increased, the crystal size increased, the thermodynamic properties tended to be stable, the ultrasonic catalytic ability was enhanced. If the Nb_2O_5 was heated more than 500 °C, the Nb_2O_5 would gradually change to the orthorhombic system.

3.7. Influence of different ultrasonic temperature on sonocatalytic degradation

$\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1, 500 °C) was used to degrade the methamphetamine hydrochloride aqueous solution at 700 W ultrasonic power for 5 h, and the degradation efficiencies at 15 °C, 35 °C and 55 °C were compared. It can be seen from Fig. 7 that the degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was 82.17% when the ultrasonic temperature was 35 °C. The degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was 59.68% when the ultrasonic temperature was 15 °C. The degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ to methamphetamine hydrochloride was only 30.49% when the ultrasonic temperature was higher at 55 °C. The above results showed that the temperature were not conducive to $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ on the degradation of methamphetamine hydrochloride no matter what too high or too low. At lower temperatures, the activity of electrons and holes in Nb_2O_5 was weak, and the reaction temperature was improved to favor the formation of electron-hole pairs. However, higher temperature condition led to electrons and holes recombination that the catalytic activity was reduced instead finally.

Fig. 3. EDX images of the prepared (a) Nb_2O_5 powder (heat treatment temperature 500 °C, heat treatment time 1 h), (b) $\text{Er}^{3+}:\text{YAlO}_3$ powder (heat treatment temperature 1100 °C, heat treatment time 2 h) and (c) $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ complex powder (the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 was 0.15:1, heat treatment temperature was 500 °C, heat treatment time 1 h).

3.8. Influence of different ultrasonic power on sonocatalytic degradation

$\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1, 500 °C) was used to compare the sonocatalytic degradation power at 420 W, 560 W and 700 W. Each sample was ultrasonicated for 5 h, followed by examination of the degradation rate of aqueous solution of methamphetamine hydrochloride. It can be seen from Fig. 8 that the sonocatalytic degradation rate of

$\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was up to 82.17% when the ultrasonic power reached 700 W under other fixed conditions. The ultrasonic degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was 70.57% when the ultrasonic power was 560 W. The degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ on the methamphetamine hydrochloride was 38.56%, and decreased by 53.07% when the ultrasonic power was 420 W. The experiments showed that the higher the ultrasonic power was the better the effect of the aqueous

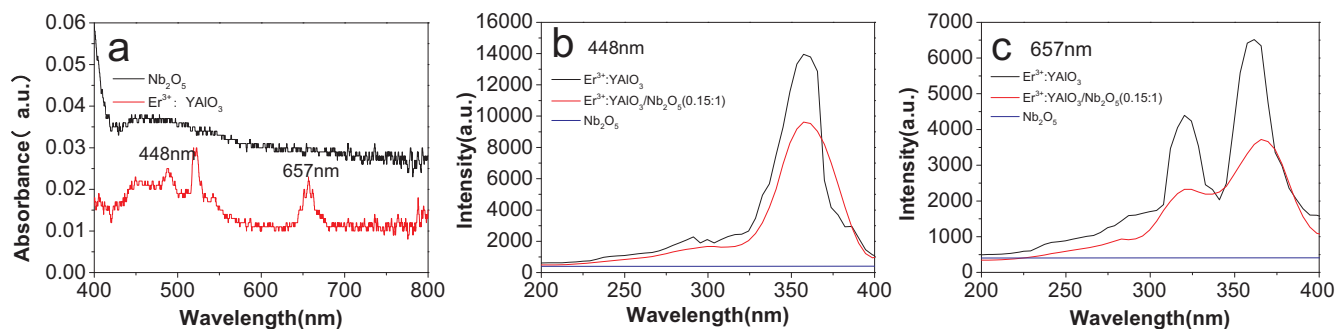


Fig. 4. UV-Vis absorption spectra and photoluminescence spectra of Nb_2O_5 , $\text{Er}^{3+}:\text{YAlO}_3$ and $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$. (a) Is the UV-visible absorption spectrum of Nb_2O_5 and $\text{Er}^{3+}:\text{YAlO}_3$. (b) Is the photoluminescence spectrum of Nb_2O_5 , $\text{Er}^{3+}:\text{YAlO}_3$ and $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1) at 448 nm. (c) Is the photoluminescence spectrum of Nb_2O_5 , $\text{Er}^{3+}:\text{YAlO}_3$ and $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1) at 657 nm.

Fig. 5. Effect of different mass ratio $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 sonocatalysts on the degradation of methamphetamine hydrochloride (a) and its reaction kinetics (b) (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

Fig. 6. Effect of different calcination temperature on sonocatalytic degradation rate of methamphetamine hydrochloride (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

solution of the methamphetamine hydrochloride.

3.9. Influence of reuse on sonocatalytic degradation of methamphetamine hydrochloride

The degradation ability of sonocatalyst composites was studied by using $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1, 500 °C). After degradation, the $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composites were recovered. The degradation ability of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composites were also studied. It can be seen from Fig. 9 that the degradation efficiency of methamphetamine hydrochloride was 82.17% when the $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composite was firstly used for the degradation of methamphetamine hydrochloride. In

Fig. 7. Effect of temperature on ultrasonic degradation rate of methamphetamine hydrochloride (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1.0 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

next four experiments, the degradation rate of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composite was stable at 78.63%, 76.58%, 75.68% and 75.39%, respectively. When $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was continuously used after the fifth time, the degradation rate of the composite material was still up to 74.71%. The data showed that $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composites had stable sonocatalytic performance and could be reused.

3.10. Gas chromatographic and gas chromatography-mass spectrometry analysis of methamphetamine hydrochloride by ultrasonic degradation

Fig. 10 was a gas chromatogram of 10 mg/L methamphetamine hydrochloride solution at different sonocatalytic degradation time. The retention time of methamphetamine hydrochloride was 5.053 min

Fig. 8. Effect of ultrasonic output power on the degradation rate of methamphetamine hydrochloride (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

Fig. 9. Investigated on used times of sonocatalyst (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

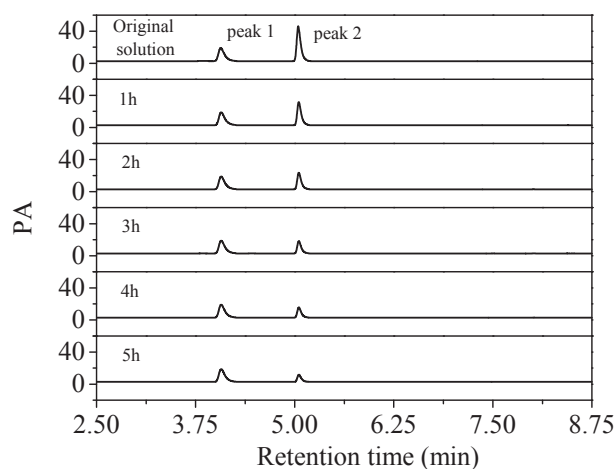


Fig. 10. Gas chromatography of methamphetamine hydrochloride solutions with different ultrasonic irradiation time (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

(peak 2), and the retention time of N, N-dimethylaniline was 4.068 min (peak 1). It can be seen from Fig. 10 that there was no other absorption peak before and after the retention time of 5.053 min, and no other new material was formed, which indicated that the methamphetamine hydrochloride was gradually mineralized by $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$

sonocatalyst. Moreover, with the extension of the time for sonocatalytic degradation, the ratio of the peak area of methamphetamine hydrochloride compared to the peak area of the internal standard was significantly decreased, indicating that methamphetamine hydrochloride molecules were destroyed by $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ composite sonocatalytic materials. After the sonocatalytic degradation 5 h, the content of methamphetamine hydrochloride had been very low, and the methamphetamine hydrochloride molecules had been degraded by 82.17%.

In order to understand the degradation products of methamphetamine hydrochloride, It was degraded with ultrasonic by $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ (0.15:1, 500 °C) composite sonocatalyst for 5 h, then it extracted with n-hexane for 500 times. The extracted n-hexane solution was analyzed by GC/MS as was shown in Fig. 11.

According to Fig. 11, methamphetamine hydrochloride peak appeared at 6.128 min, a trace of 2-phenylcyclopropanamine, amphetamine and allylbenzene was noticed at 5.367 min, 5.323 min, and 3.937 min. Other substances were not found before and after the methamphetamine peak, indicating that it was rapidly mineralized after the process of preliminary degradation.

3.11. Mechanism of sonocatalytic degradation of methamphetamine hydrochloride caused by $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder under ultrasonic irradiation

At present, there is no satisfactory explanation for the sonocatalytic degradation of drugs. Theoretical mechanisms generally believe that the mechanism of catalytic degradation is mainly due to ultrasonic cavitation effect of the resulting sonoluminescence and “hot spots”. In this paper, the possible mechanism of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ degradation is explained as follows.

Ultrasonic cavitation effect generated a sonoluminescence that can produce a wide range of light. Nb_2O_5 , as a semiconductor sonocatalyst with $E_{\text{bg}} = 3.4 \text{ eV}$, it can only absorb short wavelength light ($\lambda_{\text{max}} \leq 365 \text{ nm}$), and long wavelength light ($\lambda_{\text{max}} > 365 \text{ nm}$) cannot be absorbed. In order to increase the activity of ultrasonic catalysis Nb_2O_5 , it is necessary to supply enough energy. As shown in Fig. 12, the upconversion agent $\text{Er}^{3+}:\text{YAlO}_3$ can absorb the long wavelength light which cannot be used by Nb_2O_5 . While the short wavelength light was emitted, and it can be used Nb_2O_5 . Thus, the sonocatalytic degradation ability of Nb_2O_5 can be effectively improved. In addition, the “hot spots” up to 5000 K produced by the ultrasonic cavitation effect can destroy water molecules to produce a certain amount of hydrogen free radicals ($\cdot\text{OH}$), and can excite catalytic degradation of Nb_2O_5 as light.

Under the excitation of short wavelength light, electrons are transferred from the valence band (VB) of Nb_2O_5 to the conduction band (CB), and holes are generated on the Nb_2O_5 material. Electron-hole pairs have high energy, on the one hand, the hole can be directly decomposed drugs on the surface of Nb_2O_5 material, so that degradation was occurred. On the other hand, the role of holes and water to produce hydroxyl radicals can also be used as an indirect degradation of methamphetamine hydrochloride. At the same time, the generated electrons react with oxygen dissolved in water to produce superoxide radicals ($\cdot\text{O}_2^-$), which can also become hydrogen free radicals after a series of changes. These hydroxyl radicals with strong oxidizing ability can rapidly degrade drug molecules into CO_2 , H_2O , inorganic acids and other substances.

The ultrasonic degradation of organic substance is usually based on free radicals or cavitation reactions, which are determined by the nature of the sonocatalyst itself [45,46]. In order to understand whether the degradation of methamphetamine hydrochloride is due to free radical reactions or cavitation reactions, we designed the following experiments: We added free radical scavenger DMSO and *tert*-butanol to the methamphetamine hydrochloride-degrading flasks, respectively, and the hole trapping agent EDTA and Oxalic acid, carried out for 5 h of ultrasonic degradation. The results (in Fig. 13) showed that the

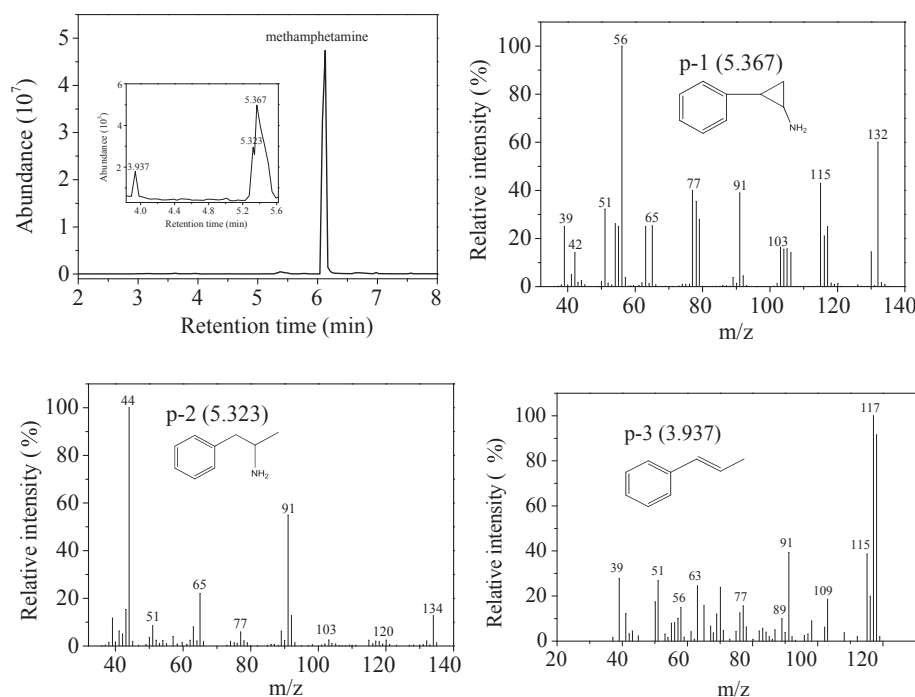


Fig. 11. Gas chromatography and mass spectrometry of the main degradation products of methamphetamine hydrochloride (ultrasonic irradiation 5 h; 1.00 g/L $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

degradation rate of methamphetamine hydrochloride was 82.17% before adding the capture agent, and the degradation rate was 16.01% and 25.38% after adding DMSO and *tert*-butanol respectively. After adding EDTA and oxalic acid, the degradation rate decreased to 71.82% and 74.92% respectively. After the addition of free radical scavenger, the degradation rate of methamphetamine hydrochloride decreased obviously, which may be due to the capture of $\cdot\text{OH}$ by free radical scavenger and the termination of the reaction. The results showed that the sonocatalytic degradation of methamphetamine hydrochloride was mainly by free radical reaction. After adding the hole scavenger, the degradation rate of methamphetamine hydrochloride decreased slightly, which indicated that the hole reaction also played a certain role. In conclusion, we can conclude that the sonocatalytic degradation of methamphetamine hydrochloride is carried out by hydroxyl radical ($\cdot\text{OH}$) reaction and hole (h^+) reaction, but is mainly by free radical ($\cdot\text{OH}$) oxidation. The possible process is as follows:

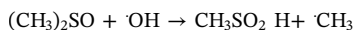
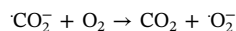
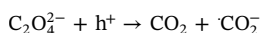
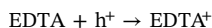
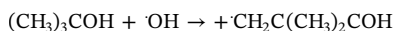


Fig. 13. Effect on sonocatalytic degradation of methamphetamine hydrochloride solution by trapping agents ($\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powder (0.15:1 $\text{Er}^{3+}:\text{YAlO}_3$ and Nb_2O_5 mass ratio heat-treated at 500 °C for 60 min), 10.00 mg/L methamphetamine hydrochloride concentration).

Fig. 12. Sonocatalytic degradation mechanism of organic pollutant in the presence of $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ powders under ultrasonic irradiation.



4. Conclusions

In this paper, the composite sonocatalyst $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was synthesized via hydrothermal method, ultrasonic dispersion and high temperature calcination method. Its degradation was carried out with 10 mg/L methamphetamine hydrochloride aqueous solution. The results showed that $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was obtained when it calcined at 500 °C for 1 h with the mass ratio of $\text{Er}^{3+}:\text{YAlO}_3$ to Nb_2O_5 (0.15:1). Under the irradiation of 700 W and 45 KHz at 35 °C, the methamphetamine hydrochloride could be decomposed into 2-phenylcyclopropanamine, Amphetamine, allylbenzene and other small molecular substances, and ultimately got mineralized. The degradation rate of methamphetamine hydrochloride was 82.17% after 5 h, moreover, the increased ultrasonic power, amount of catalyst and ultrasonic time could improve the degradation rate. The holes and hydroxyl radicals ($\cdot\text{OH}$) are identified and hydroxyl radicals ($\cdot\text{OH}$) plays a major role during the oxidation process. In addition, $\text{Er}^{3+}:\text{YAlO}_3/\text{Nb}_2\text{O}_5$ was insoluble in water, green, and reusable. The performance of methamphetamine hydrochloride degradation decreased by only 9.1% after recovery five times. It provides a new way for the harmless treatment of drugs in thinking, technology, and application prospects.

Acknowledgements

The authors greatly acknowledged Key Technology Research Project (2014JSYJA025), the Ministry of Public Security of the People's Republic of China for financial support.

References

- [1] World Drug Report 2016, United Nations Office on Drugs and Crime.
- [2] A.C. Dean, S.M. Groman, A.M. Morales, E.D. London, An evaluation of the evidence that methamphetamine abuse causes cognitive decline in humans, *Neuropsychopharmacology* 38 (2013) 259–274.
- [3] D.E. Rusyniak, Neurologic manifestations of chronic methamphetamine abuse, *Psychiatric Clin. North Am.* 36 (2) (2013) 261–275.
- [4] E.D. London, M. Kohn, A.M. Morales, M.E. Ballard, Chronic methamphetamine abuse and corticostriatal deficits revealed by neuroimaging, *Brain Res.* 1628 (2015) 174–185.
- [5] T. Lecomte, K.T. Mueser, W.M. Ewan, Predictors of persistent psychotic symptoms in persons with methamphetamine abuse receiving psychiatric treatment, *J. Nerv. Mental Dis.* 201 (2013) 1085–1089.
- [6] Annual Report on Drug Control in China 2016, Office of China National Narcotics Control commission, 2016.
- [7] Guidelines for the Safe Disposal of Unwanted Pharmaceuticals in and after Emergencies, 1999, 31 pages [E], WHO/EDM/PAR/99.2.
- [8] O.C. Bradley, A. Tarun, B. Morton, Investigating landfill leachate as a source of trace organic pollutants, *Chemosphere* 127 (2015) 269–275.
- [9] V.K. Richa, B. Arpita, A. Said, Estimating methane emissions from landfills based on rainfall, ambient temperature, and waste composition: the CLEEN model, *Waste Manage.* 46 (2015) 389–398.
- [10] T.D. Pham, B.K. Lee, C.H. Lee, The advanced removal of benzene from aerosols by photocatalytic oxidation and adsorption of Cu-TiO₂/PU under visible light irradiation, *Appl. Catal. B* 182 (2016) 172–183.
- [11] R.R. Gil, B. Ruiz, M.S. Lozano, M.J. Martín, E. Fuente, VOCs removal by adsorption onto activated carbons from biocollagenic wastes of vegetable tanning, *Chem. Eng. J.* 245 (2014) 80–88.
- [12] M. Zhang, W.J. Jiang, D. Liu, J. Wang, Y.F. Liu, Y.Y. Zhu, Photodegradation of phenol via C₃N₄-agar hybrid hydrogel 3D photocatalysts with free separation, *Appl. Catal. B* 183 (2016) 263–268.
- [13] M. Saquib, M. Muneer, Titanium dioxide mediated photocatalyzed degradation of a textile dye derivative, acid orange 8, in aqueous suspensions, *Desalination* 155 (2003) 255–263.
- [14] H. Lachheb, E. Puzenat, A. Houas, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Appl. Catal. B* 39 (2002) 75–90.
- [15] S.G. Li, C.S. Wei, J. Wang, L. Zhang, Y. Li, Y. Li, B.X. Wang, Sonocatalytic activity of

- Yb, B, Ga-codoped $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{TiO}_2$ in degradation of organic dyes, *Mater. Sci. Semicond. Process.* 26 (2014) 438–447.
- [16] J. Wang, T. Ma, Z.H. Zhang, X.D. Zhang, Y.F. Jiang, G. Zhang, G. Zhao, H.D. Zhao, P. Zhang, Investigation on transition crystal of ordinary rutile TiO₂ powder and its sonocatalytic activity, *Ultrason. Sonochem.* 14 (2007) 246–252.
- [17] H.B. Zhang, C.S. Wei, Y.Y. Huang, J. Wang, Preparation of cube micrometer potassium niobate (KNbO₃) by hydrothermal method and sonocatalytic degradation of organic dye, *Ultrason. Sonochem.* 30 (2016) 61–69.
- [18] A. Khataee, A. Karimi, S. Arefi-Oskoui, R.D.C. Soltani, Y. Hanifehpour, B. Soltani, S.W. Joo, Sonochemical synthesis of Pr-doped ZnO nanoparticles for sonocatalytic degradation of Acid Red 17, *Ultrason. Sonochem.* 22 (2015) 371–381.
- [19] J. Wang, S.Y. Zhou, J. Wang, S.G. Li, J.Q. Gao, B.X. Wang, P. Fan, Improvement of sonocatalytic activity of TiO₂ by using Yb, N and F-doped $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ for degradation of organic dyes, *Ultrason. Sonochem.* 21 (2014) 84–92.
- [20] K.P. Jyothi, S. Yesodharan, E.P. Yesodharan, Ultrasound (US), Ultraviolet light (UV) and combination (US+UV) assisted semiconductor catalyzed degradation of organic pollutants in water: Oscillation in the concentration of hydrogen peroxide formed in situ, *Ultrason. Sonochem.* 21 (2014) 1787–1796.
- [21] X. Rong, F. Qiu, J. Yan, H. Zhao, X. Zhu, D. Yang, Coupling with a narrow-band-gap semiconductor for enhancement of visible-light photocatalytic activity: preparation of Bi₂S₃/g-C₃N₄ and application for degradation of RhB, *RSC Adv.* 5 (2015) 24944–24952.
- [22] J.Q. Gao, R.Z. Jiang, J. Wang, P.L. Kang, B.X. Wang, Y. Li, K. Li, X.D. Zhang, The investigation of sonocatalytic activity of $\text{Er}^{3+}:\text{YAlO}_3/\text{TiO}_2\text{-ZnO}$ composite in azo dyes degradation, *Ultrason. Sonochem.* 18 (2011) 541–548.
- [23] J. Wang, T. Ma, Z.H. Zhang, X.D. Zhang, Y.F. Jiang, D.B. Dong, P. Zhang, Y. Li, Investigation on the sonocatalytic degradation of parathion in the presence of nanometer rutile titanium dioxide (TiO₂) catalyst, *J. Hazard. Mater. B* 137 (2006) 972–980.
- [24] J. Wang, T. Ma, Z.H. Zhang, X.D. Zhang, Y.F. Jiang, Z.J. Pan, F.Y. Wen, P.L. Kang, P. Zhang, Investigation on the sonocatalytic degradation of methyl orange in the presence of nanometer anatase and rutile TiO₂ powders and comparison of their sonocatalytic activities, *Desalination* 195 (2006) 294–305.
- [25] N. Shi, R. Yan, H. Zhou, D. Zhang, T.X. Fan, Biomass-inspired Semiconductor photocatalysts for solar degradation of organics, *Curr. Org. Chem.* 19 (2015) 521–539.
- [26] M. Rochkind, M. Pandiri, M.S. Hossain, F.W. Fossjr, K. Rajeshwar, Y. Paz, Enhancement of photoinduced visible light degradation of salicylic acid by covalently attached synthetic flavins on BiOCl semiconductor particle surfaces, *J. Phys. Chem. C* 120 (2016) 16069–16079.
- [27] J.R. Chen, F.X. Qiu, W.Z. Xua, S.S. Cao, H.J. Zhu, Recent progress in enhancing photocatalytic efficiency of TiO₂-based materials, *Appl. Catal. A* 495 (2015) 131–140.
- [28] H.B. Zhang, C.H. Ma, Y. Li, Y. Chen, C.X. Lu, J. Wang, Sol-gel-hydrothermal synthesis of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Pt-TiO}_2$ membrane and visible-light driving photocatalytic hydrogen evolution from pollutants, *Appl. Catal. A* 503 (2015) 209–217.
- [29] Y.W. Guo, Y. Li, S.G. Li, L. Zhang, Y. Li, J. Wang, Enhancement of visible-light photocatalytic activity of Pt supported potassium niobate (Pt-KNbO₃) by up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$) for hydrogen evolution from aqueous methanol solution, *Energy* 82 (2015) 72–79.
- [30] L.S. Yan, J. Zhang, X.M. Zhou, X.X. Wu, J.Y. Lan, Y.S. Wang, G. Liu, J.G. Yu, L.J. Zhi, Crystalline phase-dependent photocatalytic water splitting for hydrogen generation on KNbO₃ submicro-crystals, *Int. J. Hydrogen Energy* 38 (2013) 3554–3561.
- [31] G. Pecchi, B. Cabrera, E.J. Delgado, X. García, R. Jimenez, *Appl. Catal. A* 453 (2013) 341–348.
- [32] S. Furukawa, T. Shishido, K. Teramura, T. Tanaka, Photocatalytic oxidation of alcohols over TiO₂ covered with Nb₂O₅, *ACS Catal.* 2 (2012) 175–179.
- [33] X. Ma, Y. Chen, H. Li, X. Cui, Y. Lin, Annealing-free synthesis of carbonaceous Nb₂O₅ microspheres by flame thermal method and enhanced photocatalytic activity for hydrogen evolution, *Mater. Res. Bull.* 66 (2015) 51–58.
- [34] S. Ge, H. Jia, H. Zhao, Z. Zheng, L. Zhang, First observation of visible light photocatalytic activity of carbon modified Nb₂O₅ nanostructures, *J. Mater. Chem.* 20 (2010) 3052–3058.
- [35] B. Orel, M. Maček, J. Grdadolnik, A. Meden, In situ UV–Vis and ex situ IR spectroelectrochemical investigations of amorphous and crystalline electrochromic Nb₂O₅ films in charged/discharged states, *J. Solid State Electrochem.* 2 (1998) 221–236.
- [36] P.H. Wen, L.L. Ai, T.T. Liu, D.W. Hu, F.Y. Yao, Hydrothermal topological synthesis and photocatalyst performance of orthorhombic Nb₂O₅ rectangle nanosheet crystals with dominantly exposed (010) facet, *Mater. Design* 117 (2017) 346–352.
- [37] K.T.G. Carvalho, A.E. Nogueira, O.F. Lopes, G. Byzinskia, C. Ribeiro, Synthesis of g-C₃N₄/Nb₂O₅ heterostructures and their application in the removal of organic pollutants under visible and ultraviolet irradiation, *Ceram. Int.* 43 (2017) 3521–3530.
- [38] Y. Zhao, C. Eley, J.P. Hu, J.S. Foord, L. Ye, H.Y. He, S.C.E. Tsang, Shape-dependent acidity and photocatalytic activity of Nb₂O₅ nanocrystals with an active TT (001) surface, *Angew. Chem. Int. Ed.* 51 (2012) 3846–3849.
- [39] G.S. Li, H.B. Zhang, C.S. Wei, Y.Y. Huang, X.K. Dou, Y.D. Wang, J. Wang, Y.T. Song, Preparation of (5.0%) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Pt}(\text{TiO}_2\text{-Ta}_2\text{O}_5)$ nanocatalysts and application in sonocatalytic decomposition of ametryn in aqueous solution, *Ultrason. Sonochem.* 34 (2017) 763–773.
- [40] H.B. Zhang, Y.Y. Huang, G.S. Li, G.W. Wang, D.W. Fang, Y.T. Song, J. Wang, Preparation of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{WO}_3\text{-KNbO}_3$ composite and application in treatment of methamphetamine under ultrasonic irradiation, *Ultrason. Sonochem.* 35 (2017) 478–488.

- [41] L.N. Yin, J.Q. Gao, J. Wang, B.X. Wang, R.Z. Jiang, K. Li, Y. Li, X.D. Zhang, Enhancement of sonocatalytic performance of TiO_2 by coating $\text{Er}^{3+}:\text{YAlO}_3$ in azo dye degradation, *Sep. Purif. Technol.* 81 (2011) 94–100.
- [42] D.D. Tang, G.K. Zhang, Ultrasonic-assistant fabrication of cocoon-like Ag/AgFeO₂ nanocatalyst with excellent plasmon enhanced visible-light photocatalytic activity, *Ultrason. Sonochem.* 37 (2017) 208–215.
- [43] C.G. Alonso, A.C. Furtado, M.P. Cantão, O.A.A. Santos, N.R.C. Fernandes-Machado, Reactions over Cu/Nb₂O₅ catalysts promoted with Pd and Ru during hydrogen production from ethanol, *Int. J. Hydrogen Energy* 34 (2009) 3333–3341.
- [44] H.B. Zhang, C.S. Wei, Y.Y. Huang, G.S. Li, Q. Wu, J. Wang, Y.T. Song, Preparation of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{KNbO}_3$ composite and application in treatment of ketamine by using sonocatalytic decomposition method, *J. Hazard. Mater.* 317 (2016) 667–676.
- [45] Na. Yuan, G.K. Zhang, S. Guo, Z. Wang, Enhanced ultrasound-assisted degradation of methyl orange and metronidazole by rectorite-supported nanoscale zero-valent iron, *Ultrason. Sonochem.* 28 (2016) 62–68.
- [46] Z. Wan, G.K. Zhang, X.Y. Wu, S. Yin, Novel visible-light-driven Z-scheme $\text{Bi}_{12}\text{GeO}_{20}/\text{g-C}_3\text{N}_4$ photocatalyst: oxygen-induced pathway of organic pollutants degradation and proton assisted electron transfer mechanism of Cr(VI) reduction, *Appl. Catal. B* 207 (2017) 17–26.