

A Photocatalytic Organic Wastewater Disposing System Based on Solar Energy

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Abstract

The paper presents a photocatalytic organic wastewater disposing system, with functions of automatic examination and drainage, for disposing organic wastewater. It is based on photocatalysis and oxidization of complex TiO₂ nonmaterial, the system is made up of complex TiO₂ nonmaterial carrier units, examining and controlling unit, solar energy unit and auxiliary magnetic field unit. Light absorption diagram shows the vanishing of impurity after adequate time.

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1. INTRODUCTION

There is extraordinary superiority for Oxidation especially Ozonation of water treatment applications developed rapidly nowadays. Ozone is a strong oxidizer, with the role of a variety of organic and inorganic pollutants. The experiment was carried out by ozone-combined processes composed of preozonation conventional treatment-O₃ advanced treatment, in order to study on the degradation pattern of fouling resistance by nanosized TiO₂ modified ultra-filtration membrane catalyzed ozonation which research and application of cycle water treatment in design and optimization. Nowadays, the technique of catalytic oxidation has drawn more and more concerns in environmental pollution control mainly due to its effectiveness. The technology is based on metal oxides as a catalyst for ozonation, in the chain reaction, there is a great deal of hydroxyl radical (HO) will be produced for oxidative decomposition to remove organic pollutants that can not be direct oxidated [1].

TiO₂ has been reported to be a promising catalyst with the advantages of the physico-chemical structures and thermal stability. Compare with iron and manganese metal oxide compound, TiO₂ do not easy to present the metallic ion separation, and the particle size of nanosized TiO₂ inorganic material is from 10nm to 50nm, only about a tenth of the size of normal TiO₂ Inorganic material. Due to introducing

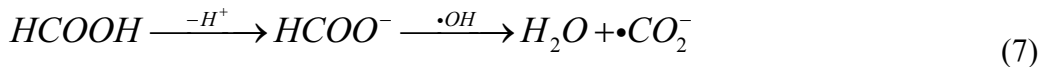
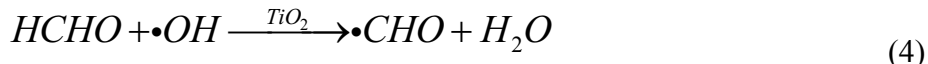
inorganic metallic compounds into organic compounds, change the polarity of membrane material and thus it makes organic pollutants easily to slough off the surface of membrane. On the other hand, nanosized TiO₂ improved net structure of organic molecule. With the particular surface effect, nanosized TiO₂ inorganic material had ascendant absorb capacity, reactivity and catalysis [2].

Nanosized TiO₂ modified ultra-filtration membrane catalyzed ozonation technology is a new method of dissolved organics removal from sewage, which can remove most of organic pollutants as well as improve performance of membrane fouling resistance. In this study, attention is concentrated on the mechanisation of catalyzed ozonation, the removal effect of ozone from organic compounds as pretreatment of membrane filtration under different technological conditions and influence of fouling resistance by nanosized TiO₂ modified ultra-filtration membrane catalyzed ozonation technology.

1.1. Operating Principle .

Scientific experiment shows [1-3] semiconductor TiO₂ will generate plenty of electrons e⁻ and photoholes h⁺ on conduction band and valence band under UV-irradiation. Dissolved oxygen adsorb on TiO₂, water molecules and others interact with electrons and holes, generate free radicals of strong oxidization such as OH, H₂O₂, O₂⁻ and so on, which can make all or nearly all organic pollutant degraded and finally generate CO₂, H₂O and other ions such as NO₃⁻, PO₄³⁻, SO₄²⁻, Cl⁻ etc by adducting, replacing, electron transferring and others with hydroxide radical of organic pollutant. Such photocatalysis oxidation can also reduce heavy metal ions and kill viruses as well as bacteria.

1.2. Reaction process [4] (Take formaldehyde light-catalytic degradation for example).



2. System construction.

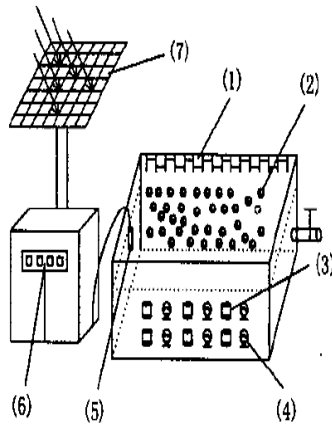


Figure 1. Schematic diagram of automatic disposal system of solar energy's photo-catalyzing organic wastewater

Figure 1 is the schematic diagram of automatic disposal system of solar energy's photo-catalyzing organic wastewater. Such system is made up of complex TiO₂ nanometer film carrier unit, solar energy unit, auxiliary magnetic field unit as well as examining and controlling unit.

2.1. Complex TiO₂ Nanometer Film Carrier Unit.

The walls and bottom of reactor is made of complex TiO₂ nanometer film carrier chips (1). Another carrier of complex TiO₂ nanometer film is the magnetic ball (2) suspending in organic wastewater. There are magnetic materials the ball with carrier out. The outside surface of carrier is complex TiO₂ nanometer film. Sol-gel methods can be used in coating film of chips and balls.

Solar Energy Unit. As for outdoor reactor system, sunlight can directly light the reactor, and its UV-light can be directly used as light source of photo-catalysis. At the same time, solar cells (7) system is designed in the system, which converts solar energy into electric energy to supply power to the UV lamp (4) installed on the bottom and side of reactor and forms the second light source of photo-catalysis. The light source is the main one of reaction system. When the energy of solar cells is not enough, circuit will supply power to realize solar-electric complement, and ensure reactor can work normally in any weather condition.

2.2. Auxiliary Magnetic Field Unit.

Electromagnet system (3) is installed on the bottom of the reactor, which supplies a discontinuous intermittent magnetic field under the action of control system. On one hand, she magnetic field is good for improving degradation rate of photo-catalytic oxidation, on the other hand, it makes the magnetic suspendballs suspending in organic wastewater ceaselessly move up and down in order to make reaction film receive fully photons, fully touch and react with organic pollutant. The quantity of magnetic suspendballs depends on quantity of disposed wastewater and volume of reactor. Because of magnetic

adsorption and control effect, the magnetic suspendballs in large-scale reactor are easy to automatically recycle, replace, wash and reuse.

2.3. Examining and Controlling Unit.

Examining and controlling unit is made up mainly of central control single chip (6) and water quality sensor (5), mainly realizes three functions:

(1) Monitor the waste water disposing index in the reactor. Realize dynamic record, start discharge magnetic valve when disposal reaches the standard. (2) Monitor the working condition of solar cells, start the circuit power supply switch to supply power to UV light source. (3) Control auxiliary magnetic field system according to design process, and realize discontinuous magnetic field and recycling and washing of magnetic suspendballs.

3. 3. EXPERIMENTAL INSTALLATION AND METHOD

3.1. Experimental Installation.

Experimental methods: Frequency Ozone Generator (Tianjin Tianning Purification equipment Invenotor SK-CFG- 5P), TOC, EDX, SEM [5]. Schematic diagram of the filtration system used in this study, ozone was generated by Frequency Ozone Generator, oxygen gas was as air supply, ozone was in the form of small air-bubbles took place in a glass reactor (1000mL) referred to as a reformer though sand core aerator into sewage (700mL). In the end the tail gas was absorbed by KI (2%).

3.2. Experimental Method.

Shimadzu TOC-V cph was used to determine TOC of sewage; Iodometric determination of ozone concentration; Observation of the membranes Micro-structure in SEM by FEI QUANTA 200 scanning electron microscope; Analysis of TiO₂ in XRD by BRUCK D8 DISCOVER spectrum analyzer.

3.3. Experimental design.

The unpaired electron of free radicals has a tendency of pairing, so most free radicals are very active, highly reactive and can form a stable molecule easily. As a reaction intermediate, hydroxyl free radical triggers chain reactions. HO • directly reacts with various organic compounds non-selectively and breaks them down into CO₂, H₂O and other harmless substances through electron transfer, electrophonic addition and dehydrogenation reaction [6]. The oxidation of HO • is a physical and chemical process, can take place under mild reaction conditions, is easier to control and the equipment is relatively simple, so it is an effective degradation of organic pollutants in wastewater. Tert-butyl alcohol is a typical quenching agent of HO • and the reaction rate constant is $5 \times 10^8 \text{ L} \cdot (\text{mol} \cdot \text{s})^{-1}$ it can react with HO • rapidly and thus compete with the oxidation of organic compounds and can't produce CO₂ and H₂O, so it is the equivalent of termination agent of ozone decomposition chain reaction [4]. Nano TiO₂ causes or promotes the reaction of ozone decomposition, so more HO • are produced in the solution or on the surface of catalyst and thus more organic compounds are oxidized [5]. HO • is good for the induction of ozone decomposition chain reaction and improve the generation of HO •. The reaction of HO • is non-selectively and the rate of the reaction is rapid, so the removal rate of TOC rises. If TiO₂ loaded in the hybrid membrane indeed catalyzes ozone and produces HO •, then the reaction will be seriously affected by tert-butyl alcohol, so we can indirectly judge whether the reaction follows the

mechanism of HO • or not by examining the impact of tert-butyl alcohol. Take 700mL water sample (water in wastewater treatment plant after primary treatment, meaning sinking sand and primary sedimentation) and add different concentrations of tert-butyl alcohol (0mg/L, 2mg/L, 5mg/L, 10mg/L), the concentration of ozone is 1.34mg/L and after aeration of ozone (1 min, 3min, 6min, 10min) take the filtrate to measure the TOC. When ozone reacts 10min, the TOC of the sample without tert-butyl alcohol is 22.3%, while the samples adding tert-butyl alcohol are 37.4% (2mg/L), 64.1% (5mg/L), 68.3% (10mg/L), we can conclude that with the increasing of tert-butyl alcohol, the degradation of organics is strongly inhibited [4]. The solution adding 2mg/L tert-butyl alcohol, the removal rate of TOC reduces 15.1 %, and with the increasing of tert-butyl alcohol, the removal rate of organics is ceaseless decreasing, 10mg/L tert-butyl alcohol makes the removal rate of TOC reduce 46% [7]. It means that in the catalytic reactions of degradation of organics, HO • is dominant, especially in the first six minutes, the inhibition of tert-butyl alcohol is obvious, and then this trend tend to be gentle for the restriction of catalyst concentration. when the concentration of tertbutyl alcohol is under certain conditions, because the catalytic ozonation is inhibited by tert-butyl alcohol added, so their organic removal rates have no significant difference. Ozone oxidation directly makes that with the increasing time of ozone reaction, the TOC concentration of original membrane and TiO₂ hybrid membrane both reduces. We can see that at the sampling points of 3min, 6min and 10min, compared with original membrane, hybrid membrane has an advantage tendency, so we suspect that enough ozone makes that a part of produced HO • isn't fully quenched[8]. The experiment we use a fixed dosage of ozone, by adjusting the oxygen flow to control the ozone concentration and ozone dosage is measured by potassium iodide reduction and sodium thiosulfate anti-titration. The greater oxygen flow, the smaller ozone concentration, through which to control the different ozone flows. Under the operating condition of 1.34mg/L ozone dosage, after aeration of 1-10min make the samples go through hybrid membrane, then record the filtrate volume every 10min and operate 120min continuously to study the flux decay rate of membrane in order to determine the minimum aeration time After the determination of minimum aeration time, adjust the oxygen flow to control the ozone dosage (1.01mg/L, 1.06mg/L, 1.34mg/L, 2.10mg/L), then filter the samples, record the volume every 5min and operate 120min continuously to determine the optimal ozone concentration according to the flux decay of membrane.

4. Experiment results

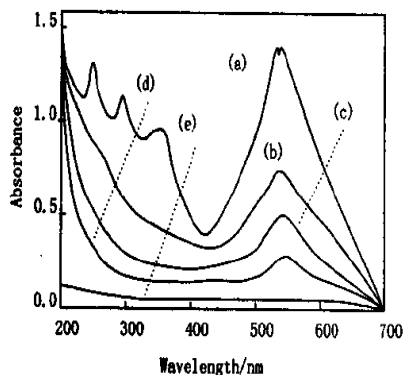
4.1. Brief Introduction to Experiment.

Use glass container as reactor; put the glass chips coated with TiO_2 / SnO_2 complex nanometer film and hollow magnetic glass balls respectively on walls and in reaction solution. 3000 ml dye X-3B solution with mass concentration of 50 mg/L (PH value 5.5). Put 2 UV bactericidal lamps of 20 W with quartz tube shields in solution as UV light source. Send air through the pipe at the bottom of reactor at speed of 20L/h. Put intermittently permanent magnet under the reactor to make intermittent magnetic field in reaction area and to make magnetic balls move up and down. After photo-catalysis reaction starts, extract 5 ml reaction solution every 15 minutes, use SHI-MADZU UV-160 UV visible spectrophotometer to measure the absorption spectrum of reaction solution. According to absorbance at maximum absorption wavelength 538 nm, apply Lambert-Beer Law to calculate the concentration of reaction solution.

4.2. Effect of Photo-catalytic Degradation.

Diagram 2 is the UV-visible spectrum of dye X-3B solution in photo-catalytic degradation. The solution has characteristic absorption peak at $\lambda=538\text{nm}$ before reaction; the intensity of absorption peak

gradually lowers with degradation reaction going. The peak completely disappears when reaction goes for about 60 min, which shows unsaturated chromophore conjugated bonds in X-3B molecules are completely broken, at the same time; the absorption peak of chromophore also complete disappears such as benzene ring and others at 200-300 nm.



(a) 0min (b) 15min (c) 30min (d) 45min (e) 60min

Figure 2. UV-visible spectrum of dye X-3B solution in photo-catalytic degradation

Repeat the above experiment with reactor in the sun. The time when characteristic absorption peak of X-3B solution at 538 nm completely disappears is about 43 min after degradation reaction starts. It shows direction sunlight can improve the speed of photo-catalytic degradation by 20%.

5. Acknowledgment

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6. References

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