Study on Water Purification Using Tungsten Trioxide Photocatalyst under Visible Light

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Abstract

This research investigates the application of photocatalytic purification of water under solar light irradiation through 3 aspects. Photocatalytic degradation of microcystin-LR (MC-LR) under simulated solar light using three classes of tungsten trioxide (WO_3)-based nanoparticles: CuO/WO_3, Pd/WO_3, and Pt/WO_3 was investigated. Photocatalytic activity was higher during the degradation of MC-LR with Pt/WO_3 than with Pd/WO_3 or CuO/WO_3. The pH value influenced the rate of degradation. The MC-LR degradation can be described by pseudo-first-order reaction kinetics, and the reaction rate increased with increasing light intensity. The influence of chloride ions and metal ions on the photocatalytic oxidation of MC-LR was also evaluated in this study. Chloride ion (Cl^-) could enhance the MC-LR degradation at a concentration of 0.02 mM and could inhibit degradation at concentrations of 0.1 mM and 0.2 mM. The presence of Cu^{2+} and Fe^{3+} improved MC-LR removal from the samples. This study suggests Pt/WO_3 photocatalytic oxidation with solar light is a promising treatment for water containing MC-LR.

The photocatalytic inhibition of algal growth under solar light was investigated using M. *aeruginosa* as the model algae and Pt/WO_3 as the photocatalyst. The experiment results shows that the algal growth was successfully controlled by the Pt/WO_3 and the total MCs was also degraded to a low level. The algae cells decreased from 1.3×10^6 to 0.1×10^6 and the total MCs concentration was dropped from 624 to 100μg/L after 6 days of photocatalytic treatment after 6 days of treatment

The comparison between photocatalytic method and electrochemical method was

investigated through the experiment of degradation of phenol. It is obvious that the reacation rate of electrochemical oxidation was much higher than that of photocatalytic oxidation. Under the optimized condition of each method, complete removal of 10mg/L phenol was achieved by photocatalytic method through 8 hours while it only took 2 hours for electrochemical method to achieve complete removal of phenol.

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Chapter 1 Introduction

1.1 Advanced oxidation processes

As recalcitrant organic pollutants continue to increase in air and wastewater streams, environmental laws and regulations become more stringent [1]. As a response, the development of newer eco-friendly methods of destroying these pollutants became an imperative task. Ultimately, research activities centered on advanced oxidation processes (AOPs) for the destruction of synthetic organic species resistant to conventional methods. AOPs rely on in situ generation of highly reactive radical species, mainly HO• by using solar, chemical or other forms of energy [2, 3]. The most attractive feature of AOPs is that this highly potent and strongly oxidizing radical allows the destruction of a wide range of organic chemical substrate with no selectivity.

1.2 Heterogeneous photocatalysis

Among AOPs, heterogeneous photocatalysis has proved to be of real interest as efficient tool for degrading both aquatic and atmospheric organic contaminants [4].Heterogeneous photocatalysis involve the acceleration of photoreaction in presence of semiconductor photocatalyst. One of the major applications of heterogeneous catalysis is photocatalytic oxidation (PCO) to effect partial or total mineralisation of gas phase or liquid phase contaminants to benign substances. Even though degradation begins with a partial degradation, the term 'photocatalytic

degradation' usually refers to complete photocatalytic oxidation or photomineralisation, essentially to CO_2, H_2O, NO_3^-, PO_4^{3-} and halide ions [5].

Photocatalysis, which was also referred to as the "Honda–Fujishima effect", was first unfolded by the pioneering research of Fujishima and Honda [6]. These workers revealed the possibility of water splitting by photoelectrochemical cell having an inert cathode and rutile titania anode. Consequently, the application of titania photocatalysis extended to environmental frontiers. Frank and Bard [7] for the first time reported the application of TiO_2 in photocatalytic oxidation of CN^- and SO_3^{2-} in aqueous medium under sunlight. Subsequent reports of photocatalytic reduction of CO_2 by Inoue et al. [8] attracted more interest in titania photocatalysis.

1.3 Fundamental principles of semiconductor photocatalysis

Heterogeneous photocatalysis has attracted constant research since its infancy considering the high number of excellent reviews and books devoted by many researchers [9]. Despite many applications, the basic photophysical principle and physical chemistry in photocatalysis is largely the same. In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (e.g., TiO_2, ZnO), an energetic light source, and an oxidizing agent such as oxygen or air. As illustrated in Fig. 1.1, only photons with energies greater than the band-gap energy (ΔE) can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants. The absorption of photons with energy lower than ΔE or longer wavelengths usually

causes energy dissipation in the form of heat. The illumination of the photocatalytic surface with sufficient energy, leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole oxidizes either the pollutant directly or water to produce hydroxyl radical $\cdot OH$, whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst (TiO_2). The activation of TiO_2 by UV light can be represented by the following steps.

$$TiO_2 + hv \ (\lambda < 387 \text{ nm}) \rightarrow e^- + h^+ \tag{1.1}$$

$$e^- + O_2 \rightarrow O_2 \bullet^- \tag{1.2}$$
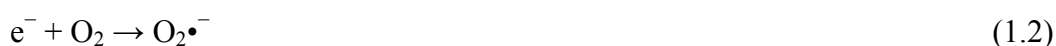
In this reaction, h^+ and e^- are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as:

Oxidative reaction:

$$h^+ + Organic(R) \rightarrow Intermediates \rightarrow CO_2 + H_2O \tag{1.3}$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \tag{1.4}$$

Reductive reaction:

$$\bullet OH + Organic \ (R) \rightarrow Intermediates \rightarrow CO_2 + H_2O \tag{1.5}$$
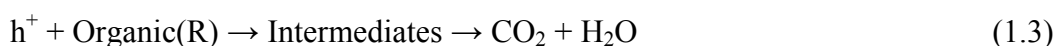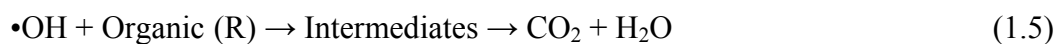
Hydroxyl radical generation by the photocatalytic oxidation process is shown in the above steps. In the degradation of organic pollutants, the hydroxyl radical generated from the oxidation of adsorbed water where it is adsorbed as OH^-, is the primary oxidant, and the presence of oxygen can prevent the recombination of an

electron–hole pair. The •OH attacks organic compounds e.g., chlorinated aromatics, aniline and nitrophenols which result in various reaction intermediates depending on the nature of the compounds. The resulting intermediates further react with •OH to produce final degradation products such as CO_2 and H_2O.

The photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, there is an electron accumulation in the CB, thereby causing an increase in the rate of recombination of e^- and h^+ [10, 11]. Thus it is of paramount importance to prevent electron accumulation in efficient photocatalytic oxidation. In photocatalysis, TiO_2 is by far the most widely studied system due to its high activity, desirable physical and chemical properties, low cost, and availability. Of three common TiO_2 crystalline forms, anatase and rutile forms have been investigated extensively as photocatalysts. Anatase has been reported to be more active as a photocatalyst than rutile. Similar oxidation pathways to those of TiO_2 are confirmed in ZnO photocatalyst including the formation of •OH radical and the direct oxidation by photogenerated holes, etc. ZnO was reported to be as reactive as TiO_2 under concentrated sunlight, since the band-gap energy of ZnO is equal to that of TiO_2, i.e., 3.2 eV. Some other metal oxides including CeO_2, SnO_2, WO_3 and CdS have also been examined for organic contaminants degradation [12-15]. At low substrate concentration, the photocatalytic degradation rate of organic compounds can be explained by a pseudo-first-order pattern, with the following equation demonstrating the relationship of C and t

$$\ln \frac{C}{C_0} = k_{obs}t \qquad (1.6)$$

where k_{obs} is the apparent reaction rate constant, t the reaction time, C_o the initial concentration of target pollutant in aqueous solution and C is the residual concentration of pollutant at time t. Different light sources such as UV lamps and solar radiation have been used in the photocatalytic degradation of various pesticides and herbicides derivatives dominant in storm water and wastewater effluent [16, 17].

1.4 History of photocatalytic materials

The discovery of water photolysis on a TiO_2 electrode by Fujishima and Honda in 1972 [6] has been recognized as the landmark event that stimulated the investigation of photonic energy conversion by photocatalytic methods, although the history of photocatalysis can be traced back to the 1960s [18-21]. Since then, intense research has been carried out on TiO_2 photocatalysis, which has been focused on understanding the fundamental principles [10,21], enhancing the photocatalytic efficiency, and expanding the scope of applications [22]. In addition to hydrogen fuel production, many other potential uses of TiO_2 photocatalysis have been identified, such as the detoxification of effluents, disinfection, superhydrophilic self-cleaning, the elimination of inorganic/organic gaseous pollutants, and the synthesis of organic fuels [23].

Unfortunately, TiO_2 is not ideal for all purposes and performs rather poorly in processes associated with solar photocatalysis. In principle, TiO_2 can utilize no more

than 5% of the total solar energy impinging on the surface of the earth due to its wide bandgap (3–3.2 eV). During the past decade, much effort has been devoted to modifying TiO_2, including energy band modulation by doping with elements such as N, C, and S [24, 25], the construction of hetero-junctions by combining TiO_2 with metals such as Pt or Pd, or other semiconductors such as NiO, RuO_2, WO_3 or CdS [26-28], and the addition of quantum dots or dyes on the TiO_2 surface for better light sensitization [29-31]. Simultaneously, the use of conventional semiconductors such as $SrTiO_3$, and WO_3 [32-34] in photocatalysis has been investigated in the search for possible alternatives to TiO_2. During the last decade, great efforts have been made to exploit complex metal oxides as novel photocatalytic materials, including niobates, tantalates, vandates and germanates, which contained the cations of d^0 or d^{10} electronic configurations such as In^{3+}, Ga^{3+}, Sb^{5+}, Bi^{5+}, and Ag^+ [35]. These novel semiconductors have proved to be among the most successful photocatalysts. For example, $NiO_x/In_{1-x} Ni_xTaO_4$ was the first material found to catalyze overall water photolysis under visible light irradiation [36]. A number of sulfides, nitrides and oxynitrides (CdS, Ta_3N_5 and TaON are among the most promising examples) have been investigated as alternative materials for visible light or solar photocatalysis [37]. In addition to classic semiconductors, polymeric C_3N_4 was recently identified as a new photocatalyst for the production of hydrogen from water under visible light [38].

After a period of lower activity in the 1980s and 1990s, interest in photocatalysis research from a scientific and engineering viewpoint has grown exponentially. This is largely due to the rapid development of nanotechnology and advanced

characterization techniques such as TEM, EELS, and XPS, which provide great opportunities for photocatalysis to realize its anticipated potential. Through persistent effort over the past forty years, remarkable progress has been made in semiconductor photocatalysis. A number of commercial photocatalytic products, including air purifiers and self-cleaning windows, are already on the market. However, for other important applications such as the production of hydrogen and organic fuel or the fabrication of photoelectrochemical solar cells, much development is still needed before commercialization is possible.

1.5 WO_3 photocatalyst

Nanostructured tungsten trioxide (WO_3), as one of the n type semiconductors with a band gap of between 2.4 and 2.8 eV, has attracted a lot of interests in photocatalysis because of its strong adsorption within the solar spectrum (≤ 500 nm), stable physicochemical properties as well as its resilience to photo corrosions [39, 40]. Under the irradiation of visible light, photoinduced electrons and holes can be produced in the conduction band and valence band of WO_3, respectively. Its good response capabilities and physico-chemical properties make it a promising material for visible-light-driven photocatalysis.

WO_3 is a visible-light-responsive photocatalyst, but its photocatalytic activity toward organic substances is low. This is due to the fact that the conduction band level of WO_3 (+0.5V vs. NHE) is more positive than the potential for the single-electron reduction of oxygen ($O_2/O_2^- = -0.56$V vs. NHE; $O_2/HO_2 = -0.13$V vs. NHE) [41]. To

solve this problem, suitable modification methods were needed.

Recently, it has been reported that platinum-loaded tungsten oxide (Pt/WO$_3$) exhibits high photocatalytic activity for the decomposition of aliphatic compounds under visible light because the surface platinum accelerates the multielectron reduction of dioxygen [42], which has more positive potential [E^0 (O$_2$/H$_2$O$_2$) = +0.695 V$_{NHE}$ for two-electron reduction and E^0(O$_2$/2H$_2$O) = +1.229 V$_{NHE}$ for four-electron reduction] than the one-electron reduction.

It is also reported that CuO can act as an effective co-catalyst for WO$_3$-catalyzed photodegradation of acetaldehyde to CO$_2$ under visible light [43]. Loading CuO on WO$_3$ also markedly promoted the photodegradation of other volatile organic compounds (VOCs), such as hexane, ethyl acetate, acetone, and diethyl ether. the redox potential [(EO$_2$(ad)/•O$_2^-$]of the O$_2$ adsorbed on CuO might be shifted to a value more positive than the potential of the bottom of the conduction band of WO$_3$, or multiple-electron reduction of O$_2$ (such as an O$_2$/H$_2$O$_2$ or O$_2$/H$_2$O redox reaction) with a more-positive redox potential compared with single-electron reduction of O$_2$ might take place on CuO co-catalyst.

Arai et al. reported that Acetaldehyde was completely oxidized to CO$_2$ over a Pd/WO$_3$ photocatalyst under fluorescent-light irradiation in a flow-type reactor, and Pd/WO$_3$ was also used to completely oxidize toluene to CO$_2$ in a batch reactor under visible-light irradiation [41]. Pd can also precede multi-electron oxygen reduction as well as Pt.

Besides, many studies on the morphology modification of Pt/WO$_3$ (e.g.,

macroporous Pt/WO_3 [44], Pt/WO_3 nanotube [40], and Pt/WO_3 hollow structure [45]) and the surface modification of WO_3 (e.g., $Cu(II)/WO_3$ [46], and $CaFe_2O_4/WO_3$ [47]) have been carried out. All previous studies using modified WO_3 demonstrated the visible light photocatalytic activity through the decomposition of organic compounds.

1.6 Aim of present research and its significance

The aim of this work is to investigate the solar light induced WO_3-based photocatalytic treatment for the purification of water. Through the treatment of organic toxin, normal recalcitrant organic contaminant and algal microorganism in water, a better comprehension of heterogeneous photocatalysis in the application of wastewater treatment could be achieved. To complete this study, a lot of efforts were needed to explore the unknown world in the field of physical chemistry science, materials science and biological science. These efforts are of special environmental and economic significance for solving several environmental problems.

1.7 References

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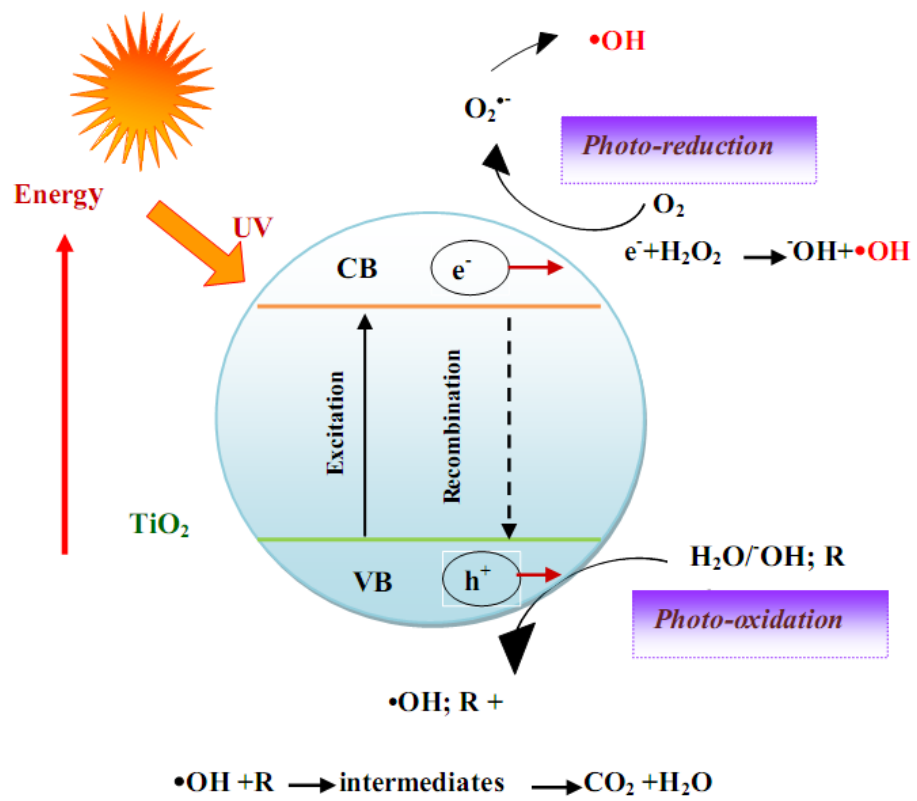
Fig. 1.1 Basic principal of photocatalysis

Chapter 2 Photocatalytic degradation of microcystin-LR in water using WO₃-based nanoparticles under simulated solar light

2.1 Introduction

An intensification of agricultural and industrial activities resulting from an increase in population has led to eutrophication in superficial freshwater bodies and has therefore induced more frequent cyanobacteria blooms worldwide. The toxins released into freshwater by cyanobacteria are well-documented [1].

Microcystins are the most commonly occurring toxins released by cyanobacteria. Microcystins are a family of cyclic heptapeptides hepatotoxins containing the unique C_{20} amino acid, 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid, which is abbreviated Adda. The most abundant and frequently detected microcystin is microcystin-LR (MC-LR), which has leucine (L) and arginine (R) in the variable positions. Microcystins are strongly hepatotoxic because they disrupt protein phosphatases 1 and 2A [2], which may promote primary liver cancer and cause the death of animals and humans. The World Health Organization (WHO) has determined a provisional guideline value of 1.0 μg/L for MC-LR in drinking water.

Various water treatment processes have been evaluated to determine their efficacy in degrading these toxins because microcystins are considered a threat to human health. However, MCs are chemically stable across a range of pH values and temperatures, due to a cyclic structure [3]; consequently, traditional water treatment

processes are unsuccessful in removing MCs [4-6].

Photocatalytic oxidation is an advanced oxidation technology that has been deemed an environmentally friendly water treatment option in recent years [7-11]. When a photocatalyst is illuminated with a light of an appropriate wavelength, pairs of electrons (e^-) and electron holes (h^+) are generated on the surface of the catalyst by photons. These pairs react with oxygen and water molecules or hydroxyl groups adsorbed on the surface of the catalyst and form highly reactive oxygen species, such as hydroxyl radicals ($\cdot OH$), superoxide ions ($\cdot O_2^-$) or hydroperoxyl radicals ($\cdot OOH$) [12]. Reactive oxygen species can nonselectively oxidize a large number of organic wastes, including dyes, pesticides, bacteria and herbicides [7-9, 13]. Previous research proved that photocatalytic oxidation with TiO_2 photocatalyst could effectively destroy MCs, even at extremely high toxin concentrations [14, 15]. However, TiO_2 has a large absorption band gap (E_g) of 3.2 eV that restricts its universal use because it can only absorb UV light [16]. Conversely, with an E_g between 2.4 eV and 2.8 eV, tungsten oxide (WO_3) is a photocatalyst that absorbs visible light irradiation up to 480 nm [11]. Compared with mixed metal oxides and doped oxides, WO_3 is inexpensive to prepare and stable in acidic and oxidative conditions, which makes it a promising material for photocatalytic applications. Previous research showed that WO_3 degradation of organic species under visible light intensified in the presence of suitable co-catalysts, such as Pt, Pd and CuO [17-19]. However, there is no literature on the photocatalytic degradation of MCs under visible light with WO_3-based catalysts.

In our study, the photocatalytic degradation of MC-LR, a model toxin, was

investigated using three types of WO$_3$-based photocatalysts: CuO/WO$_3$, Pd/WO$_3$, and Pt/WO$_3$, and simulated solar irradiation. Variations in sample parameters, such as initial pH and light intensity, were present in this study and are discussed later. Chloride ions are common in waste and natural waters, and they are important in many treatment technologies, such as breakpoint chlorination method. The presence of Cl$^-$ can enhance the performance of advanced oxidation technologies, such as the electrochemical oxidation method [20]. Therefore, it is necessary to investigate the effect of the chloride ion on the photocatalytic degradation of MC-LR. Moreover, natural waters and industrial wastes also contain dissolved metal ions, and the redox activity of metal ions may affect the rate of photocatalytic reactions. In this study, the influence of multiple metal ions on the photocatalytic oxidation of MC-LR was evaluated.

2.2 Experimental

2.2.1 Chemicals and Preparation of Photocatalysts

MC-LR standard ($\geq$95% purity; FW 995.2 g/mol) and WO$_3$ powder was purchased from Wako (Wako Pure Chemical Industries, Ltd., Japan) A 50-mg/L standard of toxin solution was prepared by adding 0.25 mg of solid toxin to 5 mL methanol. Sigma–Aldrich (Sigma-Aldrich Co. LLC., USA) supplied Pd powder with a surface area of 40 to 60 m^2/g and hexachloroplatinic acid (H$_2$PtCl$_6$•6H$_2$O). Ishihara (Ishihara Sangyo Ltd., Japan) supplied the nanoparticle compound TiO$_2$ (ST-21).

The sample of CuO/WO$_3$ was prepared by an impregnation method using WO$_3$

and $Cu(NO_3)_2$ [19]. Pd/WO_3 was prepared by the mechanical mixing of Pd and WO_3 in a ceramic mortar [21]. Pt/WO_3 was prepared by a photo deposition method using WO_3 and $H_2PtCl_6 \cdot 6H_2O$ [17].

2.2.2 Photocatalytic tests

The reactor was a 6-mL vessel equipped with a magnetic stirrer. A solar lamp (XC-100B, SERIC Ltd., Japan) was used as the irradiation source, and the light intensity was measured with a photometer (LI-250A, LI-COR Inc., USA). The photoemission spectrum was measured with an optical fiber spectrometer (USB4000, Ocean Optics Inc., USA).

An aliquot of MC-LR standard solution was added to the test solution to achieve an initial concentration of 1 mg/L. A suspension with catalyst particles was transferred to the reactor containing MC-LR to obtain a final volume of 5 ml. The initial pH was adjusted with H_2SO_4 or NaOH. Before irradiation, the suspension was stirred for 60 min in the dark to equilibrate the solution. During irradiation, samples were taken and centrifuged every 30 minutes for analysis. To evaluate the efficacy of degradation of MC-LR by different photocatalysts, a set of parallel experiments were conducted using three WO_3-based photocatayst: Pt/WO_3, Pd/WO_3 and CuO/WO_3.

2.2.3 Detection of Hydroxyl Radicals (•OH)

Photoluminescence (PL) with terephthalic acid as a probe molecule was used to detect •OH in the photocatalytic reaction system. Terephthalic acid reacts with •OH to produce highly fluorescent 2-hydroxyterephthalic acid [22].

In a beaker, a photocatalyst powder was dispersed in 20 mL of 5×10^{-4} M

terephthalic acid aqueous solution and 2×10^{-3} M NaOH. The solar lamp was used as a light source. Samples were centrifuged every 20 min for analysis.

2.2.4 Analysis

The degradation of microcystin-LR was monitored by High-performance liquid chromatography (HPLC) (Jasco-1500, Jasco, Inc., Japan) with a high-resolution diode array detector (Jasco UV-1570) set at wavelength of 238 nm. Samples were separated on a C18 column (5 m, 250 mm, 4.6 mm id) using a mobile phase of acetonitrile and Milli-Q water containing 0.01 mol/L ammonium acetate (pH 6.8; 32:68 v/v) and a flow rate of 1 mL/min. PL spectra generated by the 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer set at a wavelength of 315 nm. The pH values of the solutions were measured with a pH meter (TES-1380, TES Co., Taiwan).

2.2.5 Kinetic analysis

Photocatalytic oxidation reaction reactions have been modeled with a pseudo-first-order kinetic equation (Eq. 2.1).

$$Ln\ (C_0/C_t) = kt \tag{2.1}$$

where C_0 (mg/L) is the initial concentration of MC-LR after dark adsorption, and C_t (mg/L) is the concentration of MC-LR over reaction time t (min).

2.3 Results and Discussion

2.3.1 Photocatalytic degradation of MC-LR with various WO$_3$-based photocatalysts

As shown in Fig. 2.1, the concentration of MC-LR was virtually unchanged after 3 h of irradiation when there was no photocatalyst in the solution, thereby indicating MC-LR was stable under solar irradiation. After 3 h of irradiation, 19% of MC-LR was removed from a solution with only TiO$_2$ added, and 24% of MC-LR was removed from a solution in which only WO$_3$ was added. The modified WO$_3$-based catalysts CuO/WO$_3$ and Pd/WO$_3$ achieved 31% and 43% MC-LR removal, respectively, with 3 h of irradiation. Over 81% of MR-LR was degraded by the Pt/WO$_3$ composite within 90 min. Furthermore, the removal efficacy was 100% when the contact time was lengthened to 180 min.

Poor MC-LR removal efficiency by a solution containing only TiO$_2$ was attributable to the light source. The simulated solar lamp used in this experiment emitted light with wavelengths greater than 400 nm (Fig. 2.2), and the TiO$_2$ excitation range is less than 390 nm [16]. The low photocatalytic activity of pure WO$_3$ is because the conduction band level of WO$_3$ (+0.5V vs. NHE) is more positive than the potential for the single-electron reduction of oxygen (O$_2$/O$_2^-$ = −0.56V vs. NHE; O$_2$/HO$_2$ = −0.13V vs. NHE) [18]. Without co-catalysts, the high conduction band of WO$_3$ restricts the compound's activity with an organic compound [11].

The WO$_3$-based photocatalysts results from this study are supported by previous research. Arai et al. reported that the activity of Pd/WO$_3$ was more than twice the

activity of CuO/WO_3 in the degrading acetaldehyde, and the performance of Pt/WO_3 was better than the performance of CuO/WO_3 in the degradation of CH_3CHO [18, 19].

2.3.2 Photocatalytic degradation mechanism with WO_3-based photocatalysts

CuO, Pd, and Pt, which are co-catalysts for WO_3-induced photocatalytic reactions, can promote O_2 reduction in a multi-electron process [18, 23]. In a photocatalyic reaction, the following chain reactions have been postulated [12]:

$$Catalyst + hv \rightarrow e^- + h^+ \tag{2.2}$$

$$(O_2)\ ads + e^- \rightarrow O_2\bullet^- \tag{2.3}$$

$$H_2O \rightarrow OH^- + H^+ \tag{2.4}$$

$$O_2\bullet^- + H^+ \rightarrow HOO\bullet \tag{2.5}$$

$$HOO\bullet + e^- \rightarrow HO_2^- \tag{2.6}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{2.7}$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \tag{2.8}$$

$$OH^- + h^+ \rightarrow \bullet OH \tag{2.9}$$
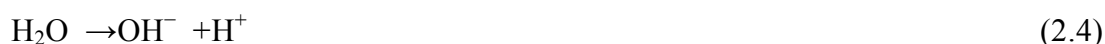
Several highly reactive oxygen species, such as $\bullet OH$, $HOO\bullet$ and $O_2\bullet^-$, are generated through the reduction of O_2 to oxidized organic compounds. Accordingly, organic compounds could be effectively degraded by WO_3 in the presence of a co-catalyst.

Photocatalytic degradation of MC-LR was initiated by the attack of hydroxyl radical on the conjugated diene structure of Adda [24], thereby indicating the primary

reactive species in MC-LR degradation was the hydroxyl radical. Kim et al. proved that the deposition of Pt on WO_3 facilitates the generation of OH radicals under visible light [25], and our experiments confirmed this phenomenon using photoluminescence (PL). Fig. 2.3 shows the spectra observed during irradiation of the Pt/WO_3 sample. At approximately 425 nm, PL intensity gradually increased with an increase in irradiation time, thereby suggesting that OH radicals are formed on the photocatalyst-water interface via photocatalytic reactions [22, 26].

Fig. 2.4 shows the plots of PL intensity for the three types of WO_3-based photocatalysts at 425 nm as a function of irradiation time. The results showed that the PL intensities by induced by simulated solar light in terephthalic acid solutions were linearly related to an increase in irradiation time. The number of OH radicals produced on the surface of the photocatalyst was proportionate to the irradiation time and obeyed zero-order reaction rate kinetics [22, 26]. Furthermore, the slopes of the lines in Fig. 2.4 describe the generation rate of OH radicals. The rate of OH radical production on the surface of Pt/WO_3 is greater than the rate of production on the surfaces of Pd/WO_3 or CuO/WO_3. Without a co-cataylsyt, WO_3 could only generate a small number of OH radicals with solar-light irradiation. Because the photocatalytic degradation of MC-LR was initiated by an OH radical [24], Pt/WO_3 is particularly effective in the photocatalytic degradation of MC-LR because of a higher OH radical production rate. Because of its efficacy, we used Pt/WO_3 in subsequent experiments.

2.3.3 Effect of initial pH on photocatalytic degradation of MC-LR

The pH affects the surface condition of catalysts and MC-LR and the generation

of hydroxyl radical in hydroxylation reactions. After 180 min of irradiation, the removal of MC-LR was 89%, 100% and 77% with pH values of 3, 6 and 10, respectively (Fig. 2.5).

Although the degradation of MC-LR was initiated by the attack of hydroxyl radical [24], the number of •OH ions should be lower at an acidic pH because hydronium ions favor the presence of an electron hole (Eq. 2.9) [27]. At low pH, MC-LR degradation would be adversely affected due to the lack of OH^- ions. The initial pH was adjusted by H_2SO_4, but Liang et al. reported that SO_4^{2-} ions have an adverse effect on the photocatalytic degradation rate [28]. Given the evidence, we can explain the lower efficiency observed in our experiment at acid pH.

The point of zero zeta-potential (PZZP) for WO_3 occurs at approximately pH 2, and WO_3 particles are negatively charged when the pH of a solution is greater than 2[25]. At pH values between 3 and 12, the carboxylic groups of MC-LR are ionized, and the molecule is negatively charged [29]. In basic conditions, negatively charged WO_3 molecules repel MC-LR and inhibit interactions between the toxins and the catalysts. Fewer interactions result in lower photocatalytic activity and a lower degradation rate. Our results are consistent with a study by Lawton et al. in which the reaction rate of photocatalytic degradation of MC-LR by TiO_2 was lowest at pH 10 [30].

2.3.4 Effect of light intensity on photocatalytic degradation of MC-LR and kinetic analysis

Light intensity influences photocatalytic activity and the energy of the

photocatalytic system. As shown in Fig. 2.6, the curves between $Ln(C_0/C_t)$ and irradiation time were consistent with first-order kinetics and had R^2 values greater than or equal to 0.99.

As expected, the photocatalytic rate constant (k) increased from 0.0149 to 0.0248 as light intensity increased from 0.2 mW/cm^2 to 0.8 mW/cm^2. As light intensity increases, the solution contains more photons and more hydroxyl radicals, and the rate of MC-LR photocatalytic degradation increases.

2.3.5 Effect of Cl⁻ on photocatalytic degradation of MC-LR

NaCl was added into the reaction solution at different concentrations, but the other experimental conditions were unchanged. The results are shown in Fig. 2.7. Without Cl⁻, 88% of MC-LR was removed after 120 min of irradiation. However, the removal efficacy increased to 94% when Cl⁻ concentration was 0.02 mM. Conversely, the removal ratio decreased to 79% and 74% when the Cl- concentrations were 0.1 mM and 0.2 mM, respectively. The results indicate that lower concentrations of Cl⁻ could enhance the degradation of toxins, but higher concentrations of Cl⁻ could inhibit degradation. Moreover, the inhibition effect was stronger at higher concentrations of Cl⁻.

In the photocatalytic process, electrons produced on the surface of the catalyst reduced O_2 molecules to $\bullet O_2^-$ radicals (Eq. 2.3), and the electron hole oxidized Cl⁻ ions to form Cl radicals ($\bullet$Cl) [31, 32].

$$Cl_{(ads)}^- + h^+ \rightarrow \bullet Cl_{(ads)} \tag{2.10}$$

Cl radicals are oxidants that can degrade organic species. Guo, J., et al. reported

that Cl- absorbed on TiO_2 molecules promoted the oxidation rate of propylene [33].

However, Cl- can also scavenge hydroxyl radicals because the reaction between HO•

and Cl- to form Cl_2 occurs quickly, and the activity of •Cl was lower than that of •OH

[28]. Consequently, when Cl- concentration increased to the point of excess, the

radical began to scavenge •OH preferentially at a rate that decreased photocatalytic

degradation of MC-LR.

2.3.6 Effect of metal ions on photocatalytic degradation of MC-LR

In this study, $Cu(NO_3)_2$ and $Fe(NO_3)_3$ were added to reaction solutions at a

concentration of 0.2 mM to investigate their effect on photocatalytic degradation of

MC-LR (Fig. 2.8). The addition of Cu^{2+} and Fe^{3+} to solution enhanced the degradation

of MC-LR. The amount of MC-LR removed from solution after 2 h of irradiation

increased from 87% to 99% in the presence of 0.2 mM Cu^{2+}, and removal increased
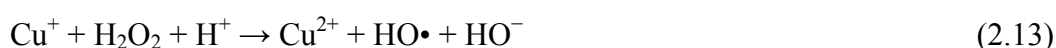
from 87% to 94% in the presence of 0.2 mM Fe^{3+}.

In photocatalytic degradation, an important factor that greatly affects the reaction

rate is the separation of photo-excited electrons and holes. Low concentrations of

liquid-phase O_2 cannot efficiently access photo-excited electrons because

photo-excited holes react with organic substances, and photo-excited electrons are

consumed through reduction of O_2 (Eq. 2.3) [12], Low photocatalytic activity in the

liquid phase is attributable to the fast recombination of excess electrons and electron

holes. Metal ions can act as a scavenger of the excess photogenerated electrons. The

consumption of electrons was achieved by the reduction of Cu^{2+} and Fe^{3+}.

$$Cu^{2+} + e^- \rightarrow Cu^+; \quad Cu^+ + e^- \rightarrow Cu \tag{2.11}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{2.12}$$

The reaction between metal ions and e^- reduced the number of undesirable electron hole combinations and increased the rate of $HO\bullet$ formation (Eq. 2.11 – Eq. 2.12) [34].

Furthermore, the metal ions can use H_2O_2 generated in Eq. 2.7 in a photo-Fenton reaction.

$$Cu^+ + H_2O_2 + H^+ \rightarrow Cu^{2+} + HO\bullet + HO^- \tag{2.13}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO\bullet + HO^- \tag{2.14}$$

The consumed form of an ion can be regenerated through Eq. 2.13 and Eq. 2.14 with photo-excited electrons, and additional $HO\bullet$ is produced and subsequently promotes the degradation of MC-LR [35, 36]. Other researchers have reported on the use of metal ions for the enhancement of photocatalytic reaction efficiency. Arai et al. used Fe^{3+}/Fe^{2+} redox for the photodegradation of organic substances with WO_3 photocatalysts [37]. Beydoun et al. reported Cu^{2+} enhanced the photocatalytic degradation of sucrose [38].

2.4 Conclusions

Under simulated solar irradiation, WO_3 degrades MC-LR more effectively in the presence of co-catalyst compared to solutions with only TiO_2 or WO_3. The highest rate of MC-LR removal occurred in solutions containing Pt/WO_3. Specifically, 1 mg/L of MC-LR was removed after 3 h of irradiation by 100 mg/L of Pt/WO_3. A neutral pH, such as a pH of 6, improved the efficacy of toxin removal. Analysis of

reaction kinetics indicated that photocatalytic MC-LR degradation followed pseudo-first-order reaction kinetics, and the reaction rate increased with an increase in light intensity. Investigation of the effect of coexistent ions on the photocatalytic oxidation of MC-LR indicated that Cl^- could enhance the MC-LR degradation at concentrations lower than 0.02 mM and inhibit degradation at concentrations of 0.1 mM and 0.2 mM. The presence of Cu^{2+} or Fe^{3+} can improve MC-LR removal. This treatment method is a promising method for enhancing the treatment of refractory organic compounds.

2.5 References

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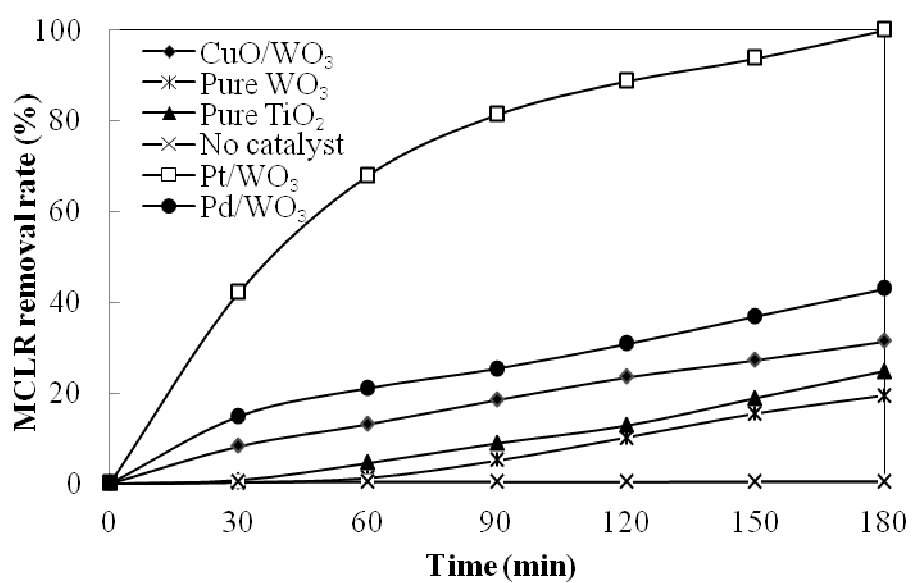
Fig. 2.1 The effect of catalysts on the efficiency of photocatalytic degradation of

MC-LR. Experimental conditions: MC-LR concentration of 1 mg/L, catalyst

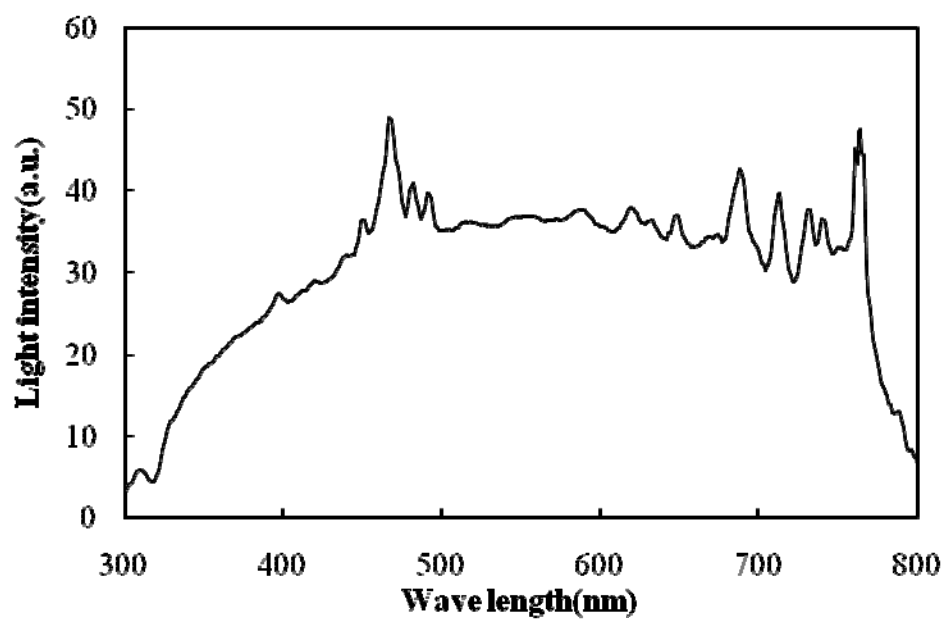concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm^2.

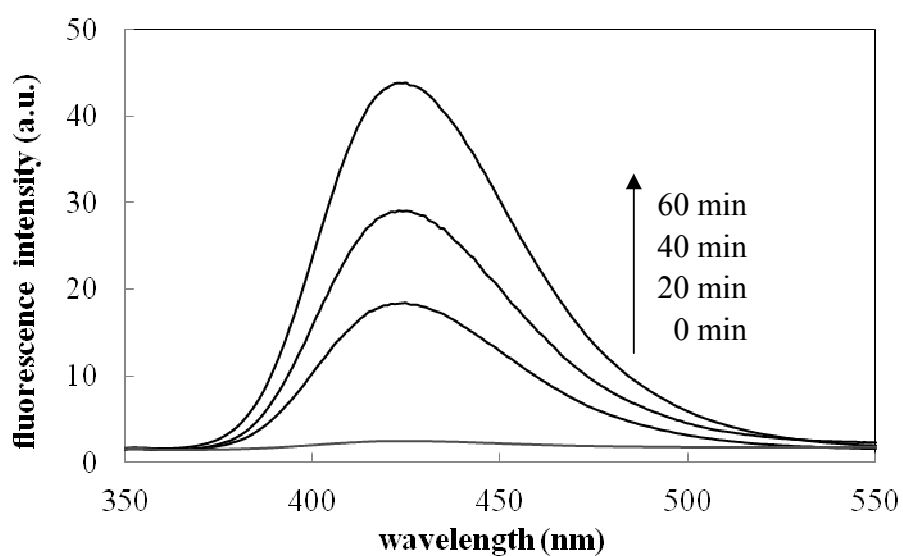Fig. 2. 2 The photoemission spectrum of the light source.

Fig. 2.3 PL spectral changes observed during irradiation of the Pt/WO$_3$ sample.

Experimental conditions: NaOH concentration of 2×10^{-3} M, terephthalic acid

concentration of 5×10^{-4} M, Pt/WO$_3$ concentration of 200 mg/L and simulated solar
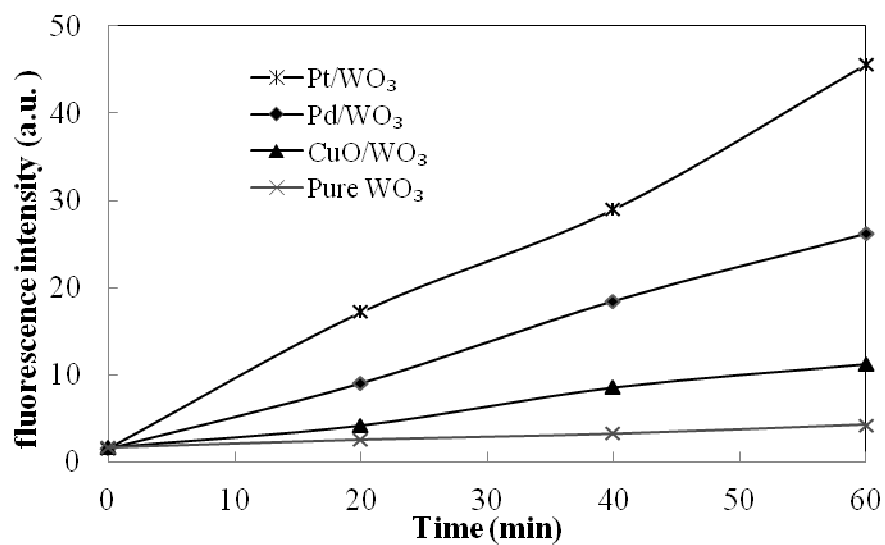
light intensity of 0.4 mW/cm^2.

Fig. 2.4 PL intensity at 42 three WO$_3$-based photocatalysts and one WO$_3$ photocatalysts as a function of irradiation time. Experimental conditions: NaOH concentration of 2×10^{-3} M, terephthalic acid concentration of 5×10^{-4} M, catalyst concentration of 200 mg/L and simulated solar light intensity of 0.4 mW/cm^2.
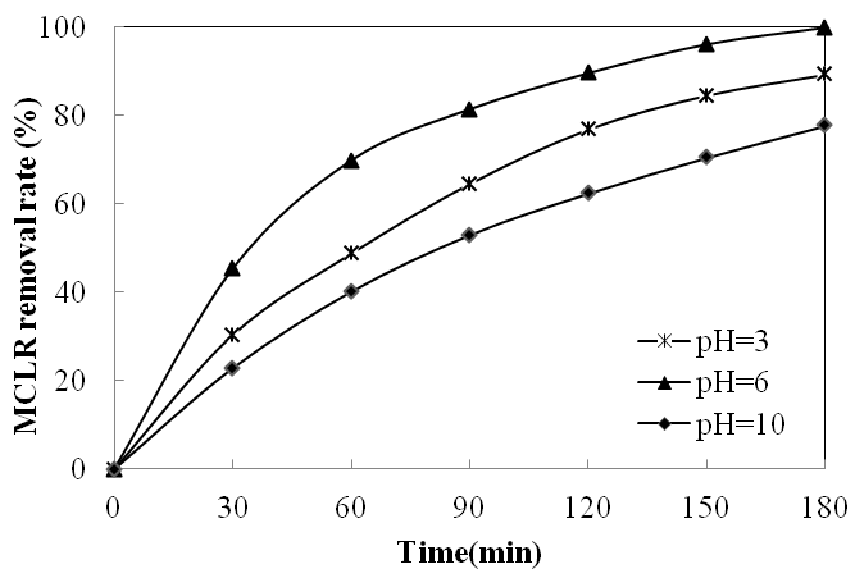
Fig. 2.5 Efficiency of photocatalytic degradation of MC-LR as a function of initial pH. Experimental conditions: MC-LR concentration of 1 mg/L, Pt/WO$_3$ concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm^2.

Fig. 2.6 Efficiency of photocatalytic degradation of MC-LR as a function of light intensity. Experimental conditions: MC-LR concentration of 1 mg/L and Pt/WO$_3$ concentration of 100 mg/L
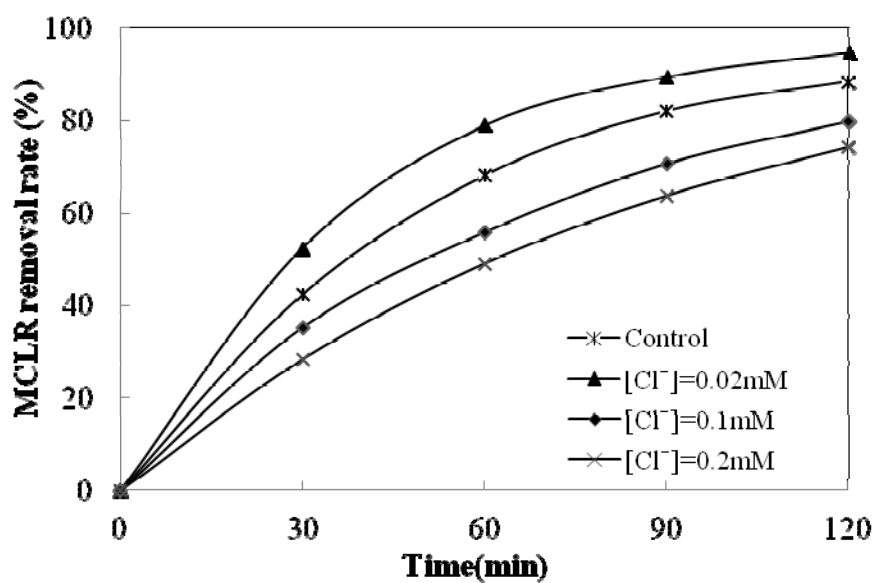
Fig. 2.7 Efficiency of photocatalytic degradation of MC-LR as a function Cl⁻

concentration. Experimental conditions: MC-LR concentration of 1 mg/L, Pt/WO$_3$

concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm^2.

Fig. 2.8 The effect of 0.2 mM of metal ions on the efficiency of photocatalytic

degradation of MC-LR. Experimental conditions: MC-LR concentration of 1 mg/L,

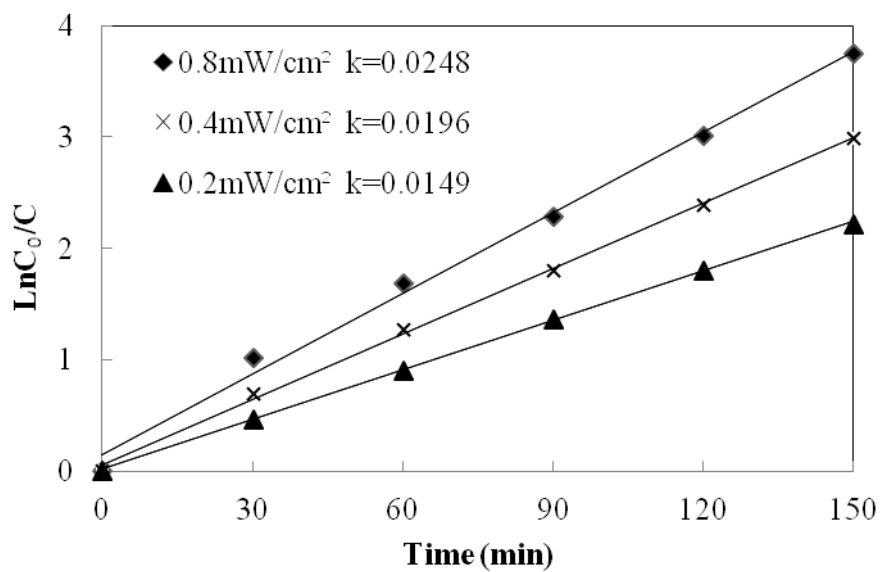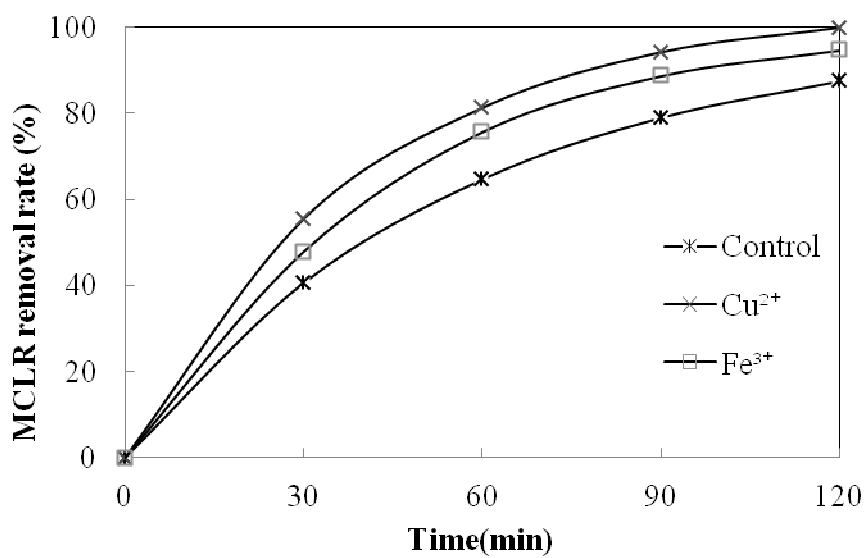Pt/WO$_3$ concentration of 100 mg/L and simulated solar light intensity of 0.4 mW/cm^2.

Chapter 3 photocatalytic inhibition of algal growth under solar light

3.1 Introduction

Cyanobacteria (blue-green algae) are photoautotrophic gram-negative bacteria that are common members of the freshwater phytoplankton community in surface waters [1]. They are considered to be a great threaten to the drinking water quality because of their ability to produce toxins and odors. The drinking water contaminated with toxic cyanobacteria could cause the death of the domestic and wild animals and the cases of human illness [2, 3]. To minimize the threat, removal of cyanobacteria has been conducted by applying physical, chemical and biological methods such as flocculation, sedimentation, floatation, and filtration technologies. However, many problems such as high cost, producing a large amount of algae sludge, and complexity of the treatment process became the hurdle when those technologies were applied to practical use. Therefore, the development of a new sustainable technology for the control of cyanobacteria is strongly demanded.

The antimicrobial activity of photocatalyic reaction by TiO_2 was first demonstrated by Matsunaga and coworkers [4], since then, photocatalysis has been shown to be capable of killing a wide range of organisms including Gram-negative and Gram-positive bacteria, including endospores, fungi, algae, protozoa and viruses, and has also been shown to be capable of inactivating prions [5-7]. Moreover recently works also reported that TiO_2-photocatalysis has the ability to inhibit the growth of

the filamentous algae, Oedogonium and Cladophora [8, 9]. However, TiO_2 has a large

absorption band gap (E_g) of 3.2 eV that restricts its universal use because it can only

absorb UV light which occupies only 3-5% of the solar spectrum [10]. From the

perspective of solar light utilization, many researchers have done a lot of works to

enhance the photocatalytic efficiency and visible light utilization of TiO_2 by

modification methods, including anionic or cationic impurity doping [11-13],

sensitization [14] and combination with smaller-bandgap semiconductors [15].

Nevertheless, the problems including complex modifying processes and low stability

of the as-prepared samples were raised and prevent the further application of TiO_2.

Compared to TiO_2, with an E_g between 2.4 eV and 2.8 eV, tungsten oxide (WO_3)

is a photocatalyst that absorbs visible light irradiation up to 480 nm [11]. Compared

with mixed metal oxides and doped oxides, WO_3 is inexpensive to prepare and stable

in acidic and oxidative conditions, which makes it a promising material for

photocatalytic applications. Previous research showed that WO_3 degradation of

organic species under visible light intensified in the presence of suitable co-catalysts,

such as Pt [16-18]. However, there is no literature on the Photocatalytic inhibition of

the algal growth under visible light with WO_3-based catalysts.

In our study, platinum was chosen as the cocatalyst to modify WO_3. It has been

confirmed that Pt/WO_3 could perform well in photocatalytic degradation of organic

substances under visible light irradiation [19]. Microcystis *aeruginosa* (M. *aeruginosa*)

was selected as test species, for it is the most common blue-green algae and easily

causes eutrophication.

3.2 Materials and methods

3.2.1 Algal culture

M. *aeruginosa* was obtained from National Institute for Environment Studies (NIES) (Ibaraki, Japan), The composition of the MA medium used in algal growth tests was listed in Table 3.1. 1L of MA medium was added to a 3L conical flask and was autoclaved at 121°C for 20 min. The cultivation was carried out in the cultivating box with illumination for 10 days. The continuous light was provided by a fluorescence lamp with an automated 12 h/12 h light/dark cycle. The light intensity during the light phase was 1500 lx. The temperature was controlled at 25±1 °C.

3.2.2 Photocatalysts preparation and characterization

Pt-loaded WO_3 sample (Pt/WO_3) was prepared by a photo deposition method [18]. An aqueous suspension containing the particulate WO_3 and $H_2PtCl_6 \bullet 6H_2O$ was exposed to visible light ($\lambda > 400$ nm) provided by a 300 W Xe lamp (LX-300F, Cermax, CA) fitted with a cutoff filter (L-42, HOYA, Japan). After 2 h of irradiation, methanol (10 vol%) was added and the suspension exposed to further irradiation for 2 h. The prepared sample was collected by centrifugation and washed twice with Milli-Q water and finally dried at 105 °C for 2 h. The prepared sample was characterized. UV-visible spectrum of the sample was recorded on a spectrophotometer (UV-2550, Shimadzu Co. Ltd., Japan). X-ray powder diffraction (XRD) measurement was carried out by using an X-ray diffractometer (Rigaku Smartlab).

3.2.3 Photocatalytic tests

Photocataltic inhibition of M. *aeruginosa* was carried out in a 200-mL beaker equipped with a magnetic stirrer. The irradiation source was the same solar lamp with an automated 12 h/12 h light/dark cycle. All the experiment equipments were placed in a clean bench to prevent the interference of dust and microorganism brought by air. 150ml of algal solution and a suspension with catalyst particles were added to the beaker for irradiation. Samples were taken every 2 days for analysis. The experiment apparatus are shown in Fig. 3.1.

3.2.4 Analysis methods

The growth of M. *aeruginosa* was evaluated by cells enumeration. The samples were diluted with Mill-Q water to obtain an appropriate cell density for microscopic counts. Then the samples were dripped to a hemocytometer and covered with a clear cover for counting. The enumeration was achieved by a microscope. To analyze the total MCs including intracellular MCs and the MCs in the solution, samples were filtered by glass microfiber filters to separate cells and MA media. Cells trapped by the filter were exposed to 5% acetic acid solution with shaking for 30 min to release the intracellular toxin. Microcystins in the acetic acid solution were absorbed by ODS column after filtration by 0.2 μm cellulose acetate filters. Then microcysins were dissolved in methanol for analysis by HPLC.

3.3 Results and discussion

3.3.1 Characterization of phoctocatalyst samples

Fig. 3.1 shows the absorption (100-reflectance) spectra for WO_3 and Pt/WO_3 powders. The absorption of WO_3 increased at approximatedly 460 nm, which is consistent with previously reported value [16]. For Pt/WO_3 sample, with the contribution of Pt doping the spectrum shows stronger broad absorption in the visible light region. The XRD patterns of WO_3 and Pt/WO_3 samples are illustrated in Fig. 3.2. Compared to tungsten oxide JCPD files (No. 43-1035) and those reported by others [23, 24], the diffraction patterns of the samples assigned those of WO_3 monoclinic structure.
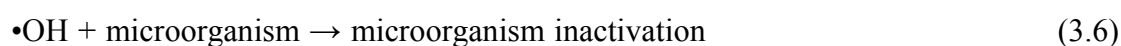
As shown, no sign of crystallite Pt is detected in the patterns with Pt/WO_3. It can be related to the fact that lower Pt concentrations lie below XRD instrumental detection limit and indicated that the Pt doping did not influence the crystal structures of WO_3.

3.3.2 Photocatalytic inhibition of algal growth under solar light

Fig. 3.4 shows the results of photocatalytic inhibition of algal growth under solar light. After 6 days of irradiation, M. *aeruginosa* in the control samples kept growing and the number of algae cells increased from 1.3×10^6 to 2.2×10^6. However, the growth of M. *aeruginosa* in the samples treated by photocatalyst was inhibited and the algae cells decreased from 1.3×10^6 to 0.1×10^6. These results show that the photocatalytic treatment had the function of inactivation of microorganisms.

It is generally believed that the inactivation of microorganisms by

photocatalylic treatment is mainly due to oxidative radicals (mainly •OH) produced by photocatalyst irradiation [20]. When a photocatalyst is illuminated with a light of an appropriate wavelength, pairs of electrons (e^-) and electron holes (h^+) are generated on the surface of the catalyst by photons. These pairs react with oxygen and water molecules or hydroxyl groups adsorbed on the surface of the catalyst and form highly reactive oxygen species, such as hydroxyl radicals (•OH), which is expected to destroy the microorganisms [21]. The existence of Pt co-catalyst can promote O_2 reduction in a multi-electron process [17, 22].

$$Pt/WO_3 \rightarrow e_{cb}^- + h_{vb}^+ \tag{3.1}$$

$$O_2 + 2e_{cb}^- + 2H^+ \rightarrow H_2O_2 \tag{3.2}$$

$$H_2O_2 \rightarrow 2\bullet OH \tag{3.3}$$

$$H_2O + h_{vb}^+ \rightarrow \bullet OH + H^+ \tag{3.4}$$

$$HO^- + h_{vb}^+ \rightarrow \bullet OH \tag{3.5}$$

$$\bullet OH + microorganism \rightarrow microorganism\ inactivation \tag{3.6}$$

3.3.3 Photocatalytic degradation of total MCs

Since the finally purpose of photocatalytic treatment is to reduce the MCs concentration in the wastewater, the total toxin concentration was analyzed in our experiment, the results were shown in Fig. 5. Without photocatalytic treatment, the total toxin concentration was increased from 624 to 741 μg/L during 6 days of irradiation. And with the existence of Pt/WO_3 photocatalyst, the total toxin concentration was decreased from 624 to 100μg/L after 6 days of photocatalytic treatment.

The protective cell structures of M. *aeruginosa* including the cell wall, the cell membrane and the organelle membranes were all destroyed by the oxidative species generated in photocatalytic process. During this process, the MCs were transferred from the inside of cells to the solution and further degraded by those oxidative species. These results further confirmed that Pt/WO_3 photocatalytic treatment is an environmental friendly way for the purification of wastewater containing algal toxin.

3.4 Conclusions

The photocatalytic inhibition of algal growth under solar light was investigated using M. *aeruginosa* as the model algae and Pt/WO_3 as the photocatalyst. The experiment results shows that the algal growth was successfully controlled by the Pt/WO_3 and the total MCs was also depredated to a low level.

The major problem in this treatment method is the recovery of the photocatalyst. Fortunately, a lot of works were already done for the immobilization of photocatalyst, such as magnetic recovery method and glass coating method. With appropriate immobilization technology, it can be sure that the photocatalytic treatment will be a promising way for in-situ control of cyanotoxins.

3.5 References

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Table　3.1 Composition of culture medium

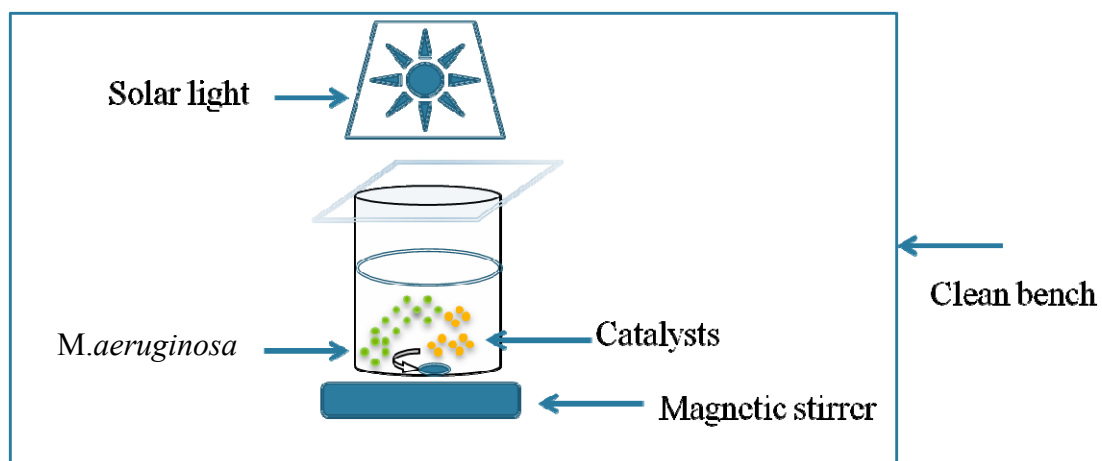| Component	Concentration (L^{-1})
$Ca(NO_3)_2 \cdot 4H_2O$	50 mg
KNO_3	100 mg
$NaNO_3$	50 mg
Na_2SO_4	40 mg
$MgCl_2 \cdot 4H_2O$	50 mg
β-Na_2glycerophosphate	100 mg
Na_2EDTA	5 mg
$FeCl_3 \cdot 6H_2O$	0.5 mg
$MnCl_2 \cdot 4H_2O$	5 mg
$ZnCl_2$	0.5 mg
$CoCl2 \cdot 6H2O$	5 mg
$Na_2MoO_4 \cdot 2H_2O$	0.8 mg
H_3BO_3	20 mg
Bicine	500 mg

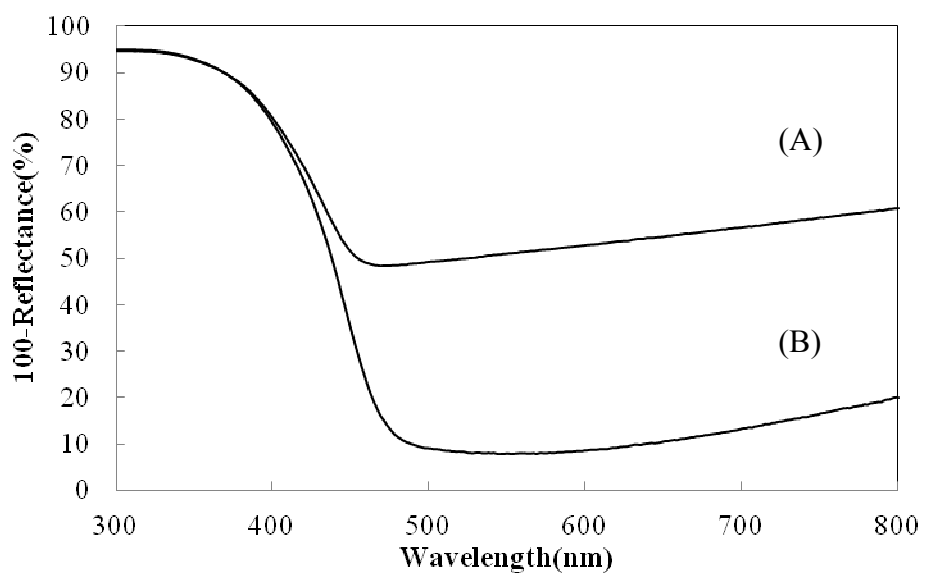Fig. 3.1 Schematic diagram of the apparatus

Fig. 3.2 Absorption spectrum of (A) Pt/WO_3 and (B) Pure WO_3, respectively.
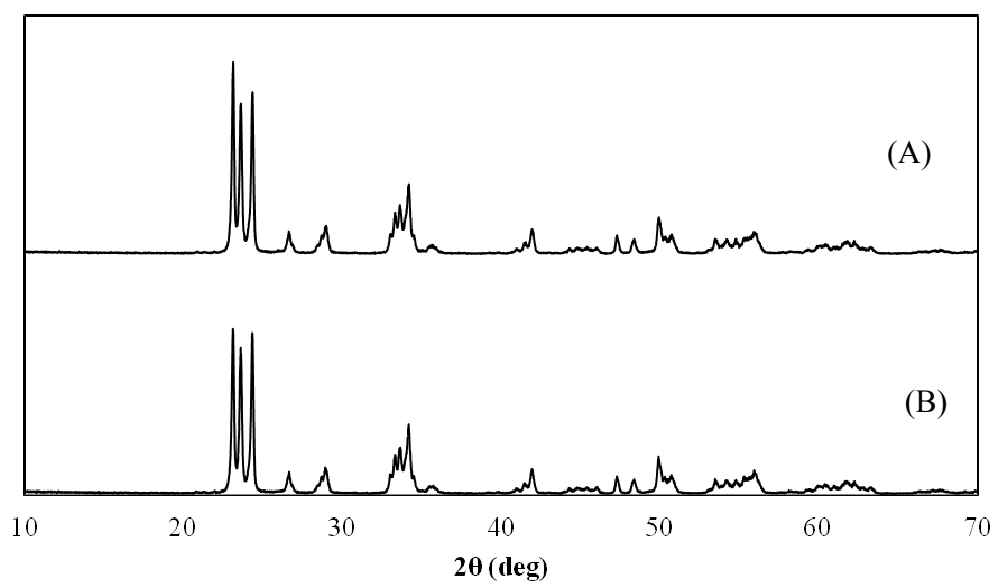
Fig. 3.3 XRD patterns of (A) pure WO_3 and (B) Pt/WO_3, respectively.

Fig. 3.4. Photocatalytic inhibition of algal growth. Experimental conditions: Catalyst concentration of 150 mg/L and simulated solar light intensity of 0.8 mW/cm^2.
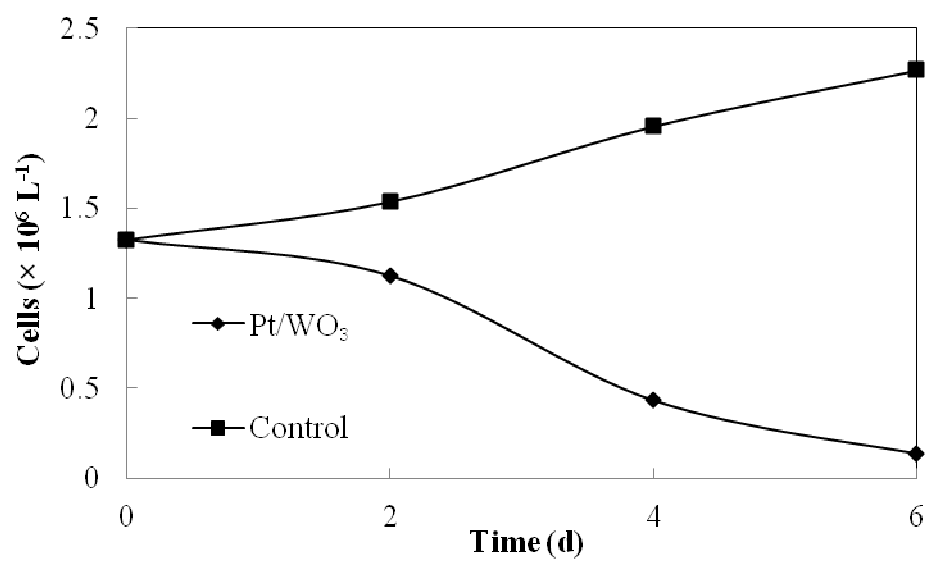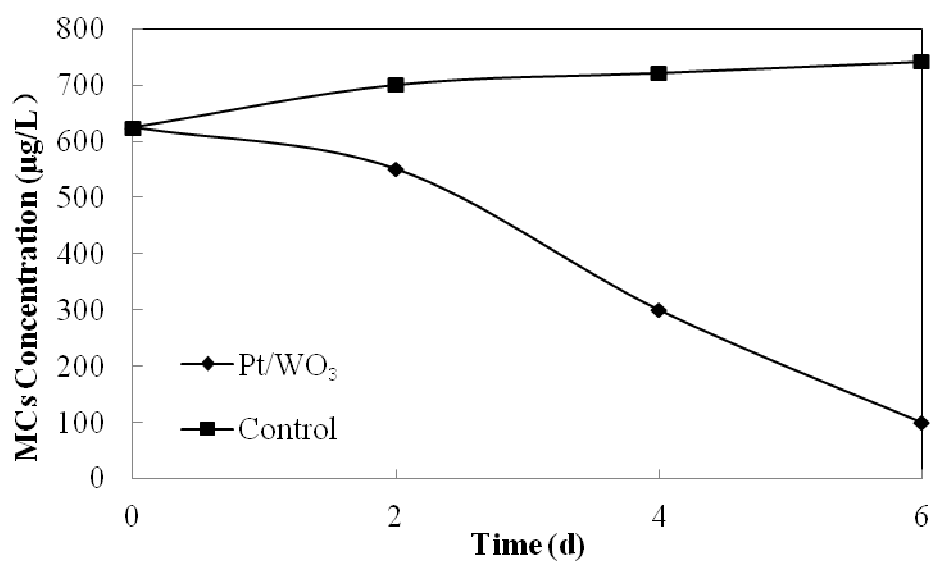
Fig. 3.5 Total MCs concentration during the photocatalytic inhibition of algal growth. Experimental conditions: Catalyst concentration of 150 mg/L and simulated solar light intensity of 0.8 mW/cm^2.

Chapter 4 Comparison of the performance between photocatalytic method and electrochemical method for the degradation of phenol

4.1 Introduction

Phenol and phenolic compounds are among the most prevalent forms of chemical pollutants and widely exist in polluted industrial wastewater in today's world. Phenol and its derivatives are widely used as raw materials and intermediates in many industries. So the Wastewater contained phenolic compounds mainly come from coking, oil refining, metallurgy, mechanical procession, glass-making, coal tar distillation, pharmaceuticals, etc [1]. Phenolic compounds cause acute toxicity, over 2mg/L phenol concentration is toxic to aquatic life and concentrations between 10 and 100mg/L can make them die within 96 h. The U.S. Environmental Protection Agency manifest that phenols represent a group of organics frequently found in various industrial effluents and reported in hazardous waste sites. Moreover according to the environmental protection rules of the Central Pollution Control Board (CPCB) the discharge limit of phenols in inland water is 1 mg/L.

Conventional wastewater treatment methods like flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis, combustion, and biological methods are incapable of removing many biorecalcitrant pollutants like phenols. This means that finding new efficient treatment methods became an imperative task.

In recent years, as one of the advanced oxidation technologies, photocatalyic oxidation has been extensive researched for the degradation and removal of highly toxic organic compounds in water purification. Among various semiconductors, titanium oxide (TiO_2), due to the excellent stability and high photoactivity under ultraviolet light, has been employed for both fundamental research and practical applications. Several researchers have studied the photocatalytic degradation of phenol in aerated suspensions of TiO_2 upon illumination with near-UV light [2, 3], However, TiO_2 has a large absorption band gap (E_g) of 3.2 eV that restricts its universal use because it can only absorb UV light [4]. Conversely, with an E_g between 2.4 eV and 2.8 eV, tungsten oxide (WO_3) is a photocatalyst that absorbs visible light irradiation up to 480 nm [11]. Compared with mixed metal oxides and doped oxides, WO_3 is inexpensive to prepare and stable in acidic and oxidative conditions, which makes it a promising material for photocatalytic applications. Previous research showed that WO_3 degradation of organic species under visible light intensified in the presence of suitable co-catalysts, such as Pt, Pd and CuO [5-7]. From now on, there are few papers about degradation of phenol under visible light with WO_3-based catalysts.

As another advanced oxidation technologies, Electrochemistry method has also attracted many attentions because of the advantages of ease of control and environmental compatibility. A lot of research works had proven that Electrochemical oxidation method is effective for the treatment of various types of wastewater including the phenolic wastewater [8-12] .Electrochemical reaction can effectively

oxidize toxic organics [9, 12-14]. With unique features such as simplicity and robustness in structure and operation, it is possible that the electrochemical process can be developed as a cost-effective technology for the treatment of aromatic pollutants, particularly for low volume applications [11]. The materials of anodes play an important role in electrochemical [14, 15]. The current efficiency of traditional electrodes is very low in organic degradation, such as using graphite and nickel [16]. At present, dimensionally stable anodes (DSA), such as SnO_2, RuO_2 or IrO_2, have been widely used for the indirect oxidation of various organic pollutants [17]. In the course of indirect electro-oxidation, hydroxyl radicals, strong oxidants that are generated on the anodic surface, can degrade organic pollutants completely. However, because of the low •OH production at the anode, it is difficult to achieve the total mineralization [11, 18]. To increase the production of active species, NaCl has been used as a supporting electrolyte [17, 19], because hypochlorous acid (HClO) can form with hydrolysis of Cl_2 gas during electrolysis [20, 21].

The pursers of this research is to do a comparison of the performance between the two kind of advanced oxidation technologies, photocatalytic oxidation method and electrochemical oxidation method, for the degradation of phenol. The degradation parameters of each method were investigated and the advantages and disadvantages of each process were demonstrated.

4.2 Experiment

4.2.1 Experimental method for electrochemical degradation of phenol

In this research, the RuO_2/Ti electrode (TOHOTEC Co. Japan) was used as anode to degrade phenol. RuO_2 is a sort of widely used electrode covering material with strong ability of the evolution of chlorine and higher oxygen evolution potential while high oxygen evolution potential can reduce the losses of electric power and increase the current efficiency. A titanium plate (TOHOTEC Co. Japan) was used as the cathode.

The electrochemical cell was a 500ml beaker, the effective area of the electrode is $43cm^2$, the distance between the electrodes was fixed at 3 cm, and a DC potentiostat was employed as power supply for electrochemical degradation. Below the beaker there is a magnetic stirrer to homogenize the solution.

An aliquot of phenol standard solution was added to the beaker to achieve an initial concentration of 10 mg/L. Different dosage of NaCl were added into the phenol solutions as the supporting electrolyte. The current densities were controlled by the DC potentiostat. At 20 min intervals, samples were drawn from the beaker for phenol analysis.

4.2.2 Experiment method for photocatalytic degradation of phenol

The photocatalyst used for phenol degradation was Pt/WO_3 which was prepared by a photo deposition method [18].

The reactor was a 6-mL vessel equipped with a magnetic stirrer. A solar lamp

(XC-100B, SERIC Ltd., Japan) was used as the irradiation source, and the light intensity was measured with a photometer (LI-250A, LI-COR Inc., USA). The photoemission spectrum was measured with an optical fiber spectrometer (USB4000, Ocean Optics Inc., USA).

An aliquot of phenol standard solution was added to the test solution to achieve an initial concentration of 10 mg/L. A suspension with catalyst particles was transferred to the reactor containing phenol to obtain a final volume of 5 ml. Before irradiation, the suspension was stirred for 60 min in the dark to equilibrate the solution. During irradiation, samples were taken and centrifuged every 30 minutes for analysis.

Phone concentration was analyzed by HPLC.

4.3 Result and discussion

4.3.1 Effect of catalyst loading on photocatalytic degradation of phenol

For the investigation of catalyst loading, a series of experiments were carried out by varying the catalyst concentration from 100 to 300 mg/L. The degradation results are shown in Fig. 4.1. It can be seen from the figure that when catalyst loading ranged from 100 to 200mg/L, the photocatalytic degradation rate increase with the increase of catalyst concentration. But increasing the catalyst concentration to 300mg/L, the degradation rate decreased.

Many studies have reported that the rates of photocatalytic degradation for

organic pollutants are affected by the number of active sites and photon-absorption ability of the catalyst used. Many authors have investigated the reaction rate as a function of catalyst loading under different experimental conditions [22, 23]. Our results are in good agreement with reported values in the literature. Chen et al. has described the possible explanation for this behavior [24]. The increase of catalyst concentration means more photons could be absorbed on the surface of catalyst and more electron/hole pairs will be generated and thus improve the formation of OH radicals for photocatalytic degradation. This fact can be confirmed from catalyst loadings less than 200mg/L. However, when catalyst loading is further increased from 200 to 300 mg/L, the performance of the catalyst decrease. It is probably that at high catalyst concentration, the aggregation of catalyst could reduce the total active surface area available for adsorbing phenol and absorbing light radiation. On the other hand, a higher concentration of catalyst creates turbidity, which is capable of reducing the penetration intensity of light radiation by the scattering effect [25]. So the optimal amount of catalyst was 200mg/L in our experiment.

4.3.2 Effect of light intensity on photocatalytic degradation of phenol

Light intensity is an important factor in influencing photocatalyic activity and normally a linear relationship between destruction rate and light intensity when the light intensity is relatively low. The effect of the light intensity was investigated by varying light intensity from 0.2 to 1.2 mW/cm^2. Fig. 4 shows the *phenol degradation curves* for different solar light intensity.

As shown in Fig. 4.2, the rate of degradation of phenol was found to increase as

light intensity increased. With the catalyst loading constant, higher light intensity means more photons available on the catalyst surface and more reactive radicals will be generated to attack the phenol molecule. However, when light intensity increased from 0.8 mW/cm^2 to 1.2 mW/cm^2, the removal rate was only enhanced slightly. The possible reason is that the number of available photons was limited to a certain amount of catalyst, when the light intensity was strong enough, more reactive species cannot be generated by increasing the light intensity. At the highest light intensity, 73% of phenol was removed in 3h of irradiation. Based on our experiment results, the optimized condition was 200mg/L of catalyst loading and 1.2 mW/cm^2 of light intensity.

4.3.3 Effect of NaCl on electrochemical degradation of phenol

Fig. 4.3 shows the performance of Ti/RuO$_2$–Pt for degradation of phenol under different dosage of NaCl. For comparison, 0.5g/L Na$_2$SO$_4$ was used as the supporting electrolyte when the NaCl was 0g/L. The concentration of phenol decreased with respect to treatment time. Without the existence of NaCl, the degradation of phenol was only 8% after 80min of electrolysis, which was similar with study of Li et al. [11], who found that with the Ti/RuO$_2$ and Pt anodes only 40% or less of the TOC was removed after a long treatment period achieved. The phenol removal increased with the increasing of NaCl dosages, 75% of phenol was removed after 80min of electrolysis with 0.3g/L NaCl, and 95% of phenol removal was achieved when the NaCl concentration was increased to 0.6g/L. However, increase the NaCl concentration to 0.9g/L, the phenol removal was only enhanced slightly, from 95% to

96%.

4.3.4 Mechanism of electrochemical oxidation of phenol

Comninellis has explained the mechanism of oxidation of organic matter at oxide anode (MO_x) [9]. In the liquid phase electrochemical oxidation, water is electrolyzed by anodic catalysis to produce adsorbed hydroxyl radicals, given as Eq. (4.1):

$$H_2O + MO_x \rightarrow MO_x[\bullet OH] + H^+ + e^-$$ (4.1)

The adsorbed hydroxyl radicals may form chemisorbed active oxygen.

$$MO_x[\bullet OH] \rightarrow MO_{x+1} + H^+ + e^-$$ (4.2)

Meanwhile, the hydroxyl radicals will react with each other to form molecular oxygen to complete the electrolysis of the water molecules.

$$MO_x[\bullet OH] \rightarrow M + O_2 + H^+ + e^-$$ (4.3)

Organic matter (R) included in wastewater are oxidized by hydroxyl radicals

$$R + MO_x[\bullet OH] \rightarrow MO_x + CO_2 + z\,H^+ + z\,e^-$$ (4.4)

$$MO_{x+1} + R \rightarrow MO_x + RO$$ (4.5)
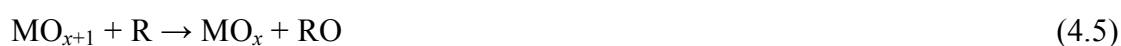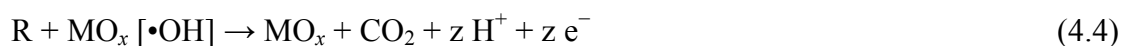
With the existence of chloride ions in the water, another strong oxidant of hypochlorite will be produced near the anode during the electrochemical process [17].

$$OH^- + Cl^- \rightarrow OCl^- + H^+ + 2e^-$$ (4.6)

The organic matter (R) are also oxidized by hypochlorite [17]

$$R + HOCl \rightarrow product + Cl^-$$ (4.7)

From the results of our experiment, it can be seen that without the existence of NaCl, the degradation of phenol was only 8% after 80min of electrolysis. This phenomenon indicated that the amount of OH radicals generated by anodic catalysis

maybe not enough for the degradation of phenol. The main active species during the electrochemical degradation is the hypochlorite. However, increase the NaCl concentration to 0.9g/L, the phenol removal was only enhanced slightly, from 95% to 96%. This phoneme could be explained by the fact that under a certain value of working current and initial concentration of phenol, the amount of chloride ions which can be used for electrochemical degradation is limited, an excessive dosage of chloride ion had no further promoting effect on phenol removal.

4.3.5 Effect of current density on electrochemical degradation of phenol

The effect of applied current density on electrochemical degradation of phenol l is shown in Fig. 4.4. The phenol removal rate during electrolysis increased with increasing current density in the range of 20-50 mA/cm^2. At the current densities of 20 mA/cm^2, 30 mA cm/cm^2, 40 mA /cm^2 and 50 mA /cm^2, the phenol removal efficiency was 76%, 86%, 94% and 95% after 80min of electrolysis, respectively. As a higher current density enhances chlorine/hypochlorite production, more phenol is likely to be oxidized. However, higher current densities will also result in the release from solution of more Cl$_2$, which is harmful to human health. Moreover, this Cl$_2$ along with the O$_2$ generated by anodic side reaction formed many large gas bubbles which need to escape from solution during experiments. These big bubbles could disturb the mass transfer and contact interface between active substances and pollutants, and hence slow down the oxidation reaction [26]. This is the main reason why the apparent rate constant at 50mA/cm^2 was only slightly greater than that at

40 mA/cm^2. Based on our experiment results, the optimized condition was 0.6g/L

NaCl and 40 mA/cm^2 of current density.

4.3.6 Comparison of the performance between photocatalytic method and electrochemical method

Fig. 4.5 shows the best performance under the optimized condition of each method. Complete removal of phenol was achieved by photocatalytic method through 8 hours while it only took 2 hours for electrochemical method to achieve complete removal of phenol.

According to the literatures, both Photocatalytic oxidation reaction and electrochemical oxidation reaction obeys a pseudo-first-order kinetic equation [27, 28] (Eq. 4.8).

$$Ln\ (C_0/C_t) = kt \hspace{4cm} (4.8)$$

where C_0 (mg/L) is the initial concentration of phenol, and C_t (mg/L) is the concentration of phenol over reaction time t (min).

The reaction constants (k) of each method are shown in Fig. 4.6. It is obvious that the reacation rate of electrochemical oxidation was much higher than that of Photocatalytic oxidation. From the experiment results we can found that for the degradation of phenol, the performance of electrochemical method was much better than the photocatalyic oxidation. But from the viewpoint of energy consumption, we can find that the two methods have their unique properties.

The main energy input of electrochemical method is the electricity power; the degradation performance can be easily enhanced by improving current density.

However, the cost of the energy consumption is also a big problem when considering the practical use. On the other hand, the main energy input of photocatalytic oxidation method is the light energy. Although the performance of photocatalytic oxidation can be enhanced by increasing the light intensity, it is not easy to control the light intensity when solar light is used as the light source.

Based on the above analysis, we come up with the conclusion that electrochemical method is appropriate for the treatment of high concentration organic wastewater. photocatalytic oxidation method is more appropriate for the in-situ control of refractory organics.

4.4 References

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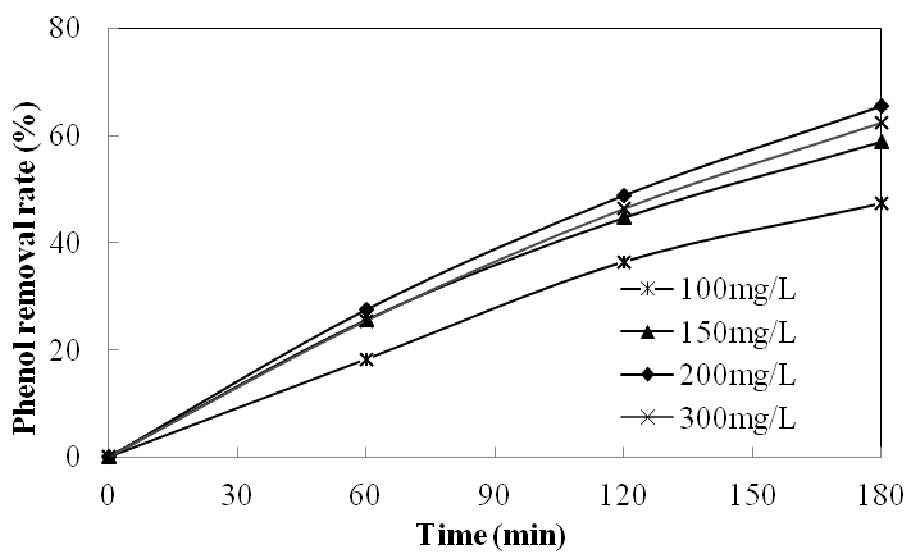
Fig. 4.1 The effect of catalyst loading on the efficiency of photocatalytic degradation of phenol. Experimental conditions: phenol concentration of 10 mg/L, simulated solar light intensity of 0.4 mW/cm^2.
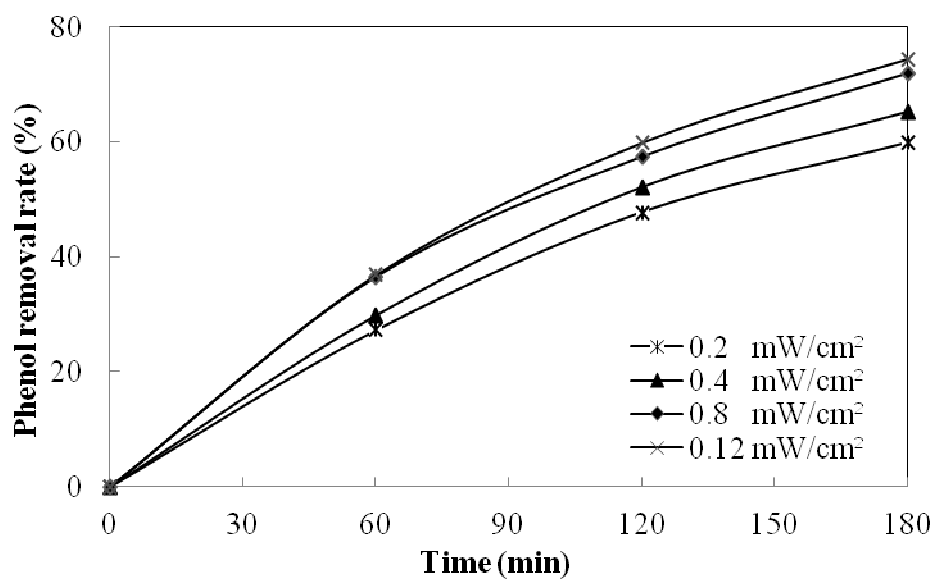
Fig. 4.2 The effect of light intensity on the efficiency of photocatalytic degradation of phenol. Experimental conditions: phenol concentration of 10 mg/L, catalyst loading of 200mg/L
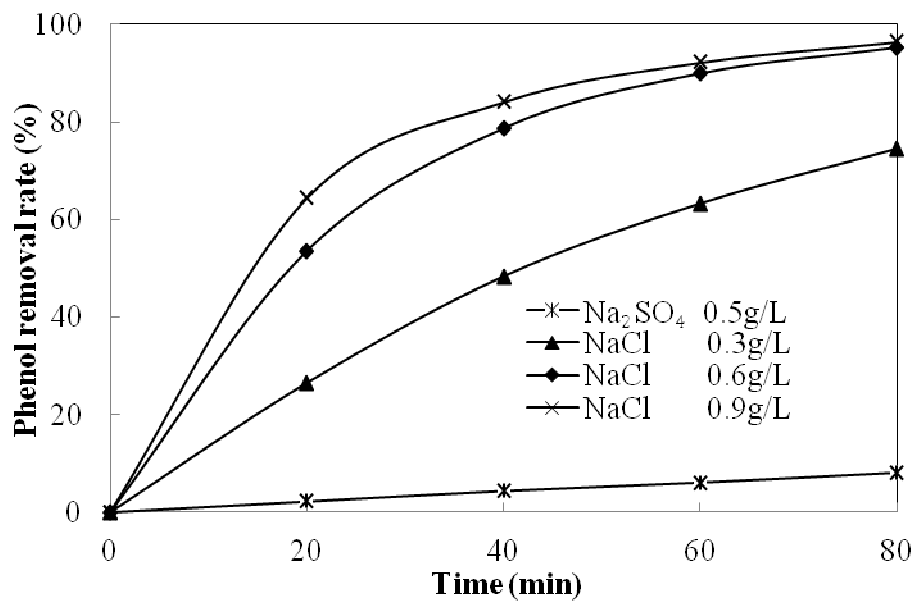
Fig. 4.3 The effect of NaCl concentration on the efficiency of electrochemical degradation of phenol. Experimental conditions: phenol concentration of 10 mg/L, current density of 40mA/cm^2
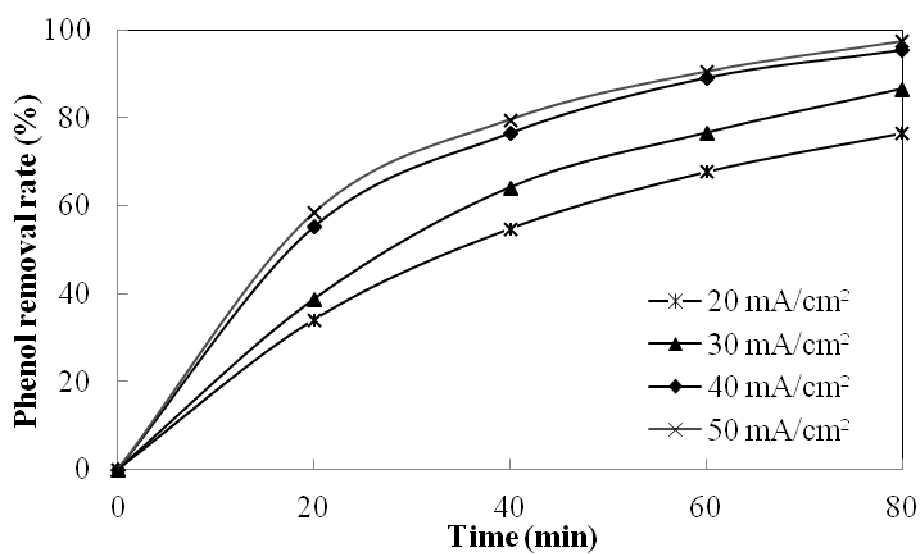
Fig. 4.4 The effect of current density on the efficiency of electrochemical degradation of phenol. Experimental conditions: phenol concentration of 10 mg/L, NaCl concentration of 0.6g/L
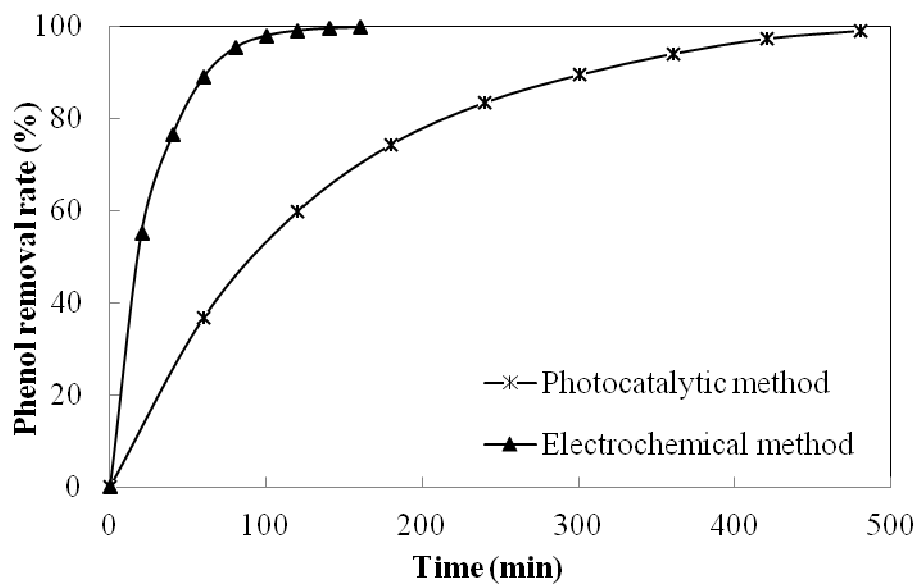
Fig. 4.5 Comparison of the performance between photocatalytic method and electrochemical method. Experimental conditions of electrochemical method: phenol concentration of 10 mg/L, NaCl concentration of 0.6g/L and current density of 40mA/cm^2. Experimental conditions of photocatalytic method: phenol concentration of 10 mg/L, catalyst loading of 200mg/L and simulated solar light intensity of 1.2 mW/cm^2.
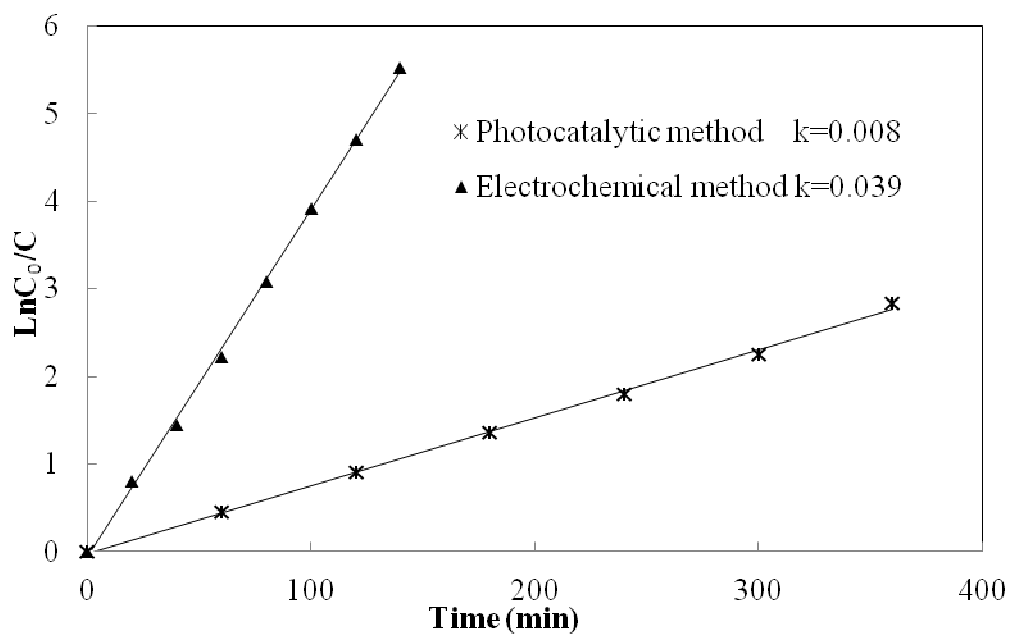
Fig. 4.6 kinetics study of photocatalytic method and electrochemical method. Experimental conditions of electrochemical method: phenol concentration of 10 mg/L, NaCl concentration of 0.6g/L and current density of 40mA/cm^2. Experimental conditions of photocatalytic method: phenol concentration of 10 mg/L, catalyst loading of 200mg/L and simulated solar light intensity of 1.2 mW/cm^2.

Chapter 5 Conclusions

This research mainly investigated the application of photocatalytic purification of water under solar light irritation through 3 aspects. The first is the degradation of cyanotoxins, microcystin-LR (MC-LR), on three kinds of WO_3-based photocatalysts under simulated solar light. It was found in this study that pure WO_3 shows low activity for MC-LR degradation due to its much positive conduction band level. Among three kinds of WO_3-based photocatalysts, Pt/WO_3 shows the best performance for the degradation. Specifically, 1 mg/L of MC-LR was removed after 3 h of irradiation by 100 mg/L of Pt/WO_3. With the existence of co-catalyst like Pd and Pt, the photocatalytic activity of WO_3 can be enhanced through the multiple-electron reduction of oxygen. The detection of proved that the solution of Pt/WO_3 generated the most amount of OH radical. Photocatalytic efficiency is affected by the initial pH of the solution, a neutral pH, such as a pH of 6, improved the efficacy of toxin removal. Analysis of reaction kinetics indicated that photocatalytic MC-LR degradation followed pseudo-first-order reaction kinetics, and the reaction rate increased with an increase in light intensity. Investigation of the effect of coexistent ions on the photocatalytic oxidation of MC-LR indicated that Cl^- could enhance the MC-LR degradation at concentrations lower than 0.02 mM and inhibit degradation at concentrations of 0.1 mM and 0.2 mM. The presence of Cu^{2+} or Fe^{3+} can improve MC-LR removal. This treatment method is a promising method for enhancing the treatment of refractory organic compounds.

To further diminish the cyanotoxins to a lower level, it is necessary to control the

growth of cyanobacteria. The second aspect is the photocatalytic inhibition of algal growth under solar light was investigated using M. *aeruginosa* as the model algae and Pt/WO$_3$ as the photocatalyst. The experiment results shows that the algal growth was successfully controlled by the Pt/WO$_3$ and the total MCs was also depredated to a low level.

The major problem in this treatment method is the recovery of the photocatalyst. Fortunately, a lot of works were already done for the immobilization of photocatalyst, such as magnetic recovery method and glass coating method. With appropriate immobilization technology, it can be sure that the photocatalytic treatment will be a promising way for in-situ control of cyanotoxins.

For further investigating photocatalytic technology in the field of refractory organic wastewater treatment, another advanced oxidation technology, electrochemical method was chosen for the comparison. In the third aspect, the comparison between photocatalytic method and electrochemical method was investigated through the degradation of phenol. It is obvious that the reaction rate of electrochemical oxidation was much higher than that of photocatalytic oxidation. From the experiment results we can found that for the degradation of phenol, the performance of electrochemical method was much better than the photocatalyic oxidation. But from the viewpoint of energy consumption, we can find that the two methods have their unique properties.

The main energy input of electrochemical method is the electricity power; the degradation performance can be easily enhanced by improving current density.

However, the cost of the energy consumption is also a big problem when considering the practical use. On the other hand, the main energy input of photocatalytic oxidation method is the light energy. Although the performance of photocatalytic oxidation can be enhanced by increasing the light intensity, it is not easy to control the light intensity when solar light is used as the light source.

Based on the above analysis, we come up with the conclusion that electrochemical method is appropriate for the treatment of high concentration organic wastewater. Photocatalytic oxidation method is more appropriate for the in-situ control of refractory organics.

In summary, the modified WO_3 nanoparticles have been successfully prepared and their photocatalytic activity for the degradation of organic toxins and refractory organic compounds and the inhibition effect in the growth of cyanobacteria were investigated. The results indicate that WO_3 can act as a promising material for solar-light driven photocatalytic technology.

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