

The Innovation of Sewage Processing Skills and the
China-Japan Cooperation on Environment (part 1)

—A Topic of Progress in Sewage Processing Skills from the
Perspective of International Technology Transfer—

SHENG Yi-ping LONG Shi-xiang CHEN Pei-lu WANG Wei

The Innovation of Sewage Processing Skills and the China-Japan Cooperation on Environment (part 1) —A Topic of Progress in Sewage Processing Skills from the Perspective of International Technology Transfer—

SHENG Yi-ping[※]

LONG Shi-xiang

CHEN Pei-lu

WANG Wei[※]

Abstract

The ways of environmental technologic innovation and its international transfer are elaborated in this paper, taking wastewater treatment as its object. Meanwhile, some empirical analysis on the current situation and the foreground of the cooperation between China and Japan are made. As the beginning part of this research, it puts emphasis on the progress in international environmental protection technology transfer.

According to different oxidative conditions and distinctive catalytic mechanism, advanced oxidation processes (AOPs) can be classified into different categories. The peculiarities, the current situation and the foreground of all types of advanced oxidative technology is shown. As for further explanation, some concrete examples of the projects processing toxic pollutants in China are introduced, which points out that as a new advanced sewage processing technology, AOPs have the merits of efficiency, general utilization and thoroughness. Also, AOPs has become the hotspot of research on the field of oxidation of anti-biodegradable pollutants.

※ College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao, Hebei 066004, China.

Therefore, it is necessary to enhance the technical co-operation, accelerate the speed of technology transfer and drive ahead the application of AOPs on a much larger scale.

Keywords : Wastewater treatment, Environmental technologic innovation, Advanced oxidation processes, Technology transfer

0 Introduction

With the development of industry and economy throughout the world in the past several decades, both the amounts and types of organic pollutants released into water have increased rapidly. Therefore, the removal of this substance from aqueous solutions is utterly important. The classical biological treatment processes are non-efficiency in the presence of these non-biodegradable and toxic pollutants. Therefore, more powerful treatment methods differentiated from the classical biological treatment methods are required. Among a variety of treatment processes, the advanced oxidation processes (AOPs) have attracted great attention throughout the last two decades due to their ability that allows reaching the total mineralization of these biorefractory and toxic pollutants. Water pollution has become a cosmopolitan issue. In order to develop water treatment technique and to improve its quality, many researchers of different countries have being working diligently.

Advanced oxidation processes (AOPs) can be broadly defined as the water treatment techniques based on in situ generation of hydroxyl radicals ($\bullet\text{OH}$). The $\bullet\text{OH}$ radicals are very powerful oxidizing agents whose standard potential ($E^0 = 2.80 \text{ V}$) is only less than that of fluorine ($E^0 = 2.87 \text{ V}$), so that they can react unselectively with organic pollutants until their total conversion into CO_2 , water and inorganic ions. Over the past three decades, the research and development

concerning AOPs has been extended mainly for two reasons, namely: (1) the diversity of technologies involved and (2) the areas of potential application. Because the production of $\bullet\text{OH}$ radical does not involve the use of harmful chemical reagents which may be hazardous for the environment, AOPs can be seen as the environment-friendly techniques. Depending on the characteristics of the wastewater to be treated and the treatment objective itself, AOPs can be employed either alone or coupled with other physicochemical and biological processes. According to the mechanisms responsible for organic matter oxidation and the catalytic conditions, the main AOPs can be approximately divided as follows:

- (1) methods based on Fenton reaction;
- (2) methods based on photoelectrocatalysis;
- (3) methods based on ozonation;
- (4) methods based on ultrasonic sound;
- (5) wet air oxidation.

1 Methods Based on Fenton Reaction

1.1 Fenton Oxidation

The catalytic decomposition of hydrogen peroxide (H_2O_2) by ferrous ion (Fe^{2+}) was first reported by Fenton⁽¹⁾. Fenton found that tartaric acid could be oxidized in hydrogen peroxide aqueous solution of low pH ($\text{pH} = 2\text{-}5$) in the presence of ferrous ion. Thereafter, an acidic aqueous solution containing hydrogen peroxide and ferrous ion is called as Fenton's reagent and the reaction between hydrogen peroxide and ferrous ion is named as Fenton reaction. Huang et al⁽²⁾ discussed the advantages and disadvantages of AOPs and suggested that the processes like Fenton methods are the most promising technologies for the treatment of biorefractory and toxic organic pollutants in waste stream. The Fenton oxidation is based on the electron transfer between hydrogen peroxide and ferrous ion,

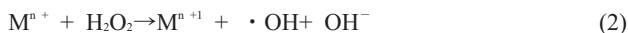
which acts as a homogenous catalyst, producing $\bullet\text{OH}$ radicals that can non-selectively degrade organic pollutants in waste stream. Fenton reaction can be described by the following equation:



Kim et al⁽³⁾ reported that the BOD/COD value of landfill leachate oxidized by Fenton's reagent increased from 0.1 to 0.4 and its biodegradation characteristic was improved. Xiao et al⁽⁴⁾ investigated the degradation of nitrobenzene wastewater with Fenton's reagent and found the BOD/COD value of the treated wastewater rising from 0.068 to 0.86. Li et al⁽⁵⁾ studied the degradation of dye model wastewater containing 9 kinds of different reactive dyes and found that under selective experimental conditions the color removal efficiency of the treated wastewater was by 95%, the COD removal efficiency was 65%~85% and the TOC removal efficiency was by 70%. Zhang et al⁽⁶⁾ did research on the effect of various factors on the degradation of PAP wastewater in a Fenton system and found that under the optimal operating condition the removal efficiency of PAP was 96%~98%, the removal efficiency of chroma was nearly 100%. The advantages of Fenton method are easy to handle and operate, using simpler apparatus and mild reaction conditions. Fenton reaction can be conveniently employed to treat a wide variety of organic compounds in surface waters as well as industrial effluents. The combination of Fenton process, which is used as either a pretreatment step or a final purifying step in an integrated process for the treatment of biorefractory and toxic organic pollutants, with biological treatment process can increase removal efficiency and decrease total operation coat of the integrated treatment process. The combination of Fenton process with other physicochemical treatment process, such as electrolysis, ultrasound and UV radiation, could increase oxidizing power and extend application area of Fenton method.

1.2 Fenton-Like Oxidation

Though its high COD removal efficiency and environmental friendliness, Fenton process is restricted by its long reaction time and more dosage of reagent needed for the treatment of wastewater polluted by organic compounds. In order to decrease the amount of metal ions needed for the catalytic decomposition of hydrogen peroxide, researchers⁽⁷⁻¹⁰⁾ investigated the usage of other metal ions, such as Co^{2+} , Mn^{2+} , Cu^{2+} and Ag^+ instead of Fe^{2+} in reaction (1), constituting so-called Fenton-like process according to reaction (2):



Where, M in the equation (2) stands for metal. The results in the area have shown that Co^{2+} , Mn^{2+} , Cu^{2+} and Ag^+ can all catalyze the decomposition of hydrogen peroxide. Using Co^{2+} instead of Fe^{2+} , the amount of metal ions needed in the catalytic reaction (2) is far more less and the reaction rate higher, but the price of cobaltic salts is higher than that of ferrous salts. While using Mn^{2+} , Cu^{2+} or Ag^+ instead of Fe^{2+} , the rate of reaction (2) can also be enhanced at some degree, but the effect is not as good as using Co^{2+} . In addition, the immobilization of Fe^{2+} on a heterogeneous matrix has also attracted researcher's attention. Fe^{2+} was immobilized on bentonite used as substrate by ions exchange or other techniques to fabricate solid catalyst for heterogeneous Fenton reaction, which could avoid the secondary pollution resulted from excess Fe^{2+} in the treated effluent^(11, 12). The immobilization of iron ions and / or other transition metal ions on a heterogeneous substrate has become one of the directions of the Fenton process.

1.3 Electro-Fenton Oxidation

It has been illuminated that the conventional Fenton process can also be modified by the combination with electrolysis process, namely electro-Fenton. In an

electro-Fenton reactor, an electrode usually made of carbonaceous materials, which mainly include graphite, reticulated vitreous carbon, carbon felt, activated carbon and activated carbon fiber, is used as cathode, and either a dissolvable stainless steel (iron) electrode or an inert platinum electrode is used as anode. H_2O_2 can be electro-generated continuously on the surface of the cathode made of carbonaceous materials from a two-electron reduction of dissolved oxygen through the reaction (3):



Fe^{2+} is either electro-generated through the electrochemical reaction (4) when a dissolvable iron anode is used or externally added when an inert platinum anode is used.



H_2O_2 electro-generated and Fe^{2+} either electro-generated or externally added into the electro-Fenton system react rapidly with each other to generate $\bullet\text{OH}$ radicals and Fe^{3+} through the reaction (1). It is obvious that Fenton's reagent is formed in the electro-Fenton system by H_2O_2 electro-generated from the reaction (3) and Fe^{2+} electro-generated from the reactions (4) or externally added, jointly.

The standard potential of the couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^0=0.77\text{V}$) is slightly higher than that of the couple $\text{O}_2/\text{H}_2\text{O}_2$ ($E^0=0.69\text{V}$), so, when dissolved oxygen is reduced to H_2O_2 on cathode surface, Fe^{3+} can also be reduced to Fe^{2+} on same cathode surface, namely Fe^{2+} is regenerated according to the electrochemical reaction (5). Due to the rate constant of the reaction (5) usually tends to be much little, the amount of the Fe^{2+} regenerated is usually negligible compared with Fe^{2+} electro-generated from reaction (4).



Because both H_2O_2 and Fe^{2+} can be electro-generated continuously, electro-Fenton reaction can also occur continuously in an electro-Fenton system.

The efficiency of generation of H_2O_2 on a cathodic surface depends mainly on the material from which the cathode is made and the preparing technique with which the cathode is prepared, so the preparing techniques of cathodes could be one of the most critical problems in an electro-Fenton process. Sheng et al⁽¹³⁾ summarized some of the main electrodes used as cathodes in the electro-Fenton processes, proposed a method for the preparation of electrode made from graphite power modified with HNO_3 and H_2PO_4 , and they also investigated main factors influencing the activity and life time of the electrode.

Due to the reaction (1) between Fe^{2+} and H_2O_2 yielding Fe^{3+} and the rate constant of the reaction (5) being usually much little, the amount of Fe^{3+} will continuously increase, inducing the excess of Fe^{3+} in an electro-Fenton system. The excessive ferric ions will combined with hydroxide ions in aqueous solution to form hydroxyl complexes. These hydroxyl complexes have very strong absorption and flocculation function and thus can absorb dissolved and colloidal pollutants in waste stream to form bigger floccules. Pollutants are removed by their homogeneous degradation with $\bullet\text{OH}$ radicals generated from reaction (1) and their parallel coagulation with the hydroxyl complexes precipitate. This process is known as peroxi-coagulation method. Enric Brillas⁽¹⁴⁾ studied the degradation of chlorophenoxy and chlorobenzoic herbicides in an acidic aqueous medium by the peroxi-coagulation method. The results showed that pollutants were efficiently removed by mineralization and coagulation, and both degradative paths compete at a low current but coagulation predominates at higher currents. Daneshvar⁽¹⁵⁾ researched the decolorization of orange II by an electrocoagulation process and found that under the experimental conditions decolorization efficiency of orange II was by 98%, COD removal efficiency was by 84%.

Compared with Fenton process the main advantages of electro-Fenton process are: (1) the fresh H_2O_2 aqueous solution produced from electrochemical reactions

has higher reaction activity, and the hazards in the transportation and the store of concentrated H_2O_2 can be avoided; (2) Fe^{2+} can partly be regenerated on cathode surface, inducing a less amount of sludge; (3) the treatment process is easier to operate.

2 Methods Based on Photoelectrocatalysis

2.1 Electrochemical Oxidation

Electrochemical oxidation over a reactive anode in the presence of suitable electrolytes has been employed for the decontamination of various organic-containing effluents^(16, 17). The mechanisms responsible for organic matter electrochemical degradation are: (1) direct anodic oxidation on an anode surface where the pollutants are adsorbed on the anode and destroyed by an anodic electron transfer reaction; (2) indirect anodic oxidation on an anode surface where the pollutants adsorbed on the anode are destroyed by $\bullet\text{OH}_{\text{abs}}$; (3) indirect oxidation in the bulk solution, which is mediated by the oxidants such as $\bullet\text{OH}$ that are formed electrochemically. On anode surface with high-oxygen overpotential H_2O is oxidized and $\bullet\text{OH}_{\text{abs}}$ is generated from the reaction (6)



The key operating parameters dictating the performances of an electrochemical system are the characteristics of working electrode, the types of supporting electrolytes and the applied currents. However, for a long time, due to lack of appropriate materials needed for preparation of highly reactive anode, the removal efficiency of electrochemical method was not cheering and the energy need was high, therefore the application of electrocatalytic oxidation subjected to restricted. At the present time, the researches are mainly focused on the development of the materials needed for preparation anode with high reactive activity and long life. The anodes made of Ti-based alloys overcome shortcomings of conventional

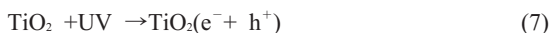
anodes made of graphite, platinum, TiO_2 , IrO_2 , PbO_2 , etc, and thus have been widely applied in water purification. Polcaro⁽¹⁸⁾ fabricated Ti-SnO_2 and Ti-PbO_2 anode with thermal deposition and electro-deposition methods, respectively, and investigated the electrochemical degradation of 2-chlorophenol on both the anodes. The results showed that the toxic compound could be more effectively degraded on Ti-SnO_2 anode, with treated effluent only containing a little biodegradable oxalic acid. Fockedeey et al⁽¹⁹⁾ prepared the three-dimensional Sb-doped SnO_2 -coated titanium foam anodes and treated phenol wastewater with the electrode, indicating that the charge consumption necessary is only 6.3 kA h/kg phenol and the energy consumption is about 5 kWh/kg COD. In recent years, boron-doped diamond (BDD) anodes have received growing attention for pollutants oxidation since they exhibit significant chemical and electrochemical stability, good conductivity as well as they achieve increased rates of mineralization with very high current efficiencies^(20, 21). The study results have demonstrated that many biorefractory compounds such as phenol, naphthol, etc can be completely mineralized with high current efficiency, even close to 100%, using BDD anodes. Sires et al⁽²²⁾ reported that although clofibric acid electro-oxidation over Pt was three times faster than over BDD, the latter was far more effective for complete mineralization to carbon dioxide and water. This is due to that some carboxylic acid with less molecular weight generated during oxidation can not completely mineralized on Pt, but can be completely oxidized to CO_2 , H_2O and inorganic salts on BDD.

2.2 Photochemical Oxidation

1972, Fujishima et al⁽²³⁾ reported photocatalytic decomposition of water carried out with a system in which a TiO_2 semiconductor electrode was exposed to near-UV light (<415 nm). 1977, Frank et al⁽²⁴⁾ showed heterogeneous photocatalytic oxidation of cyanide ion in aqueous solution with TiO_2 powder catalyst. Ever

since, there has been increasing interest in the environmental applications of photocatalysis. At present, photocatalytic oxidation of organism-polluted water with TiO₂ catalyst has been one of most energetic fields in environmental science. The main photocatalysts used in photocatalytic oxidation are TiO₂, ZnO, WO₃, CdS, ZnS, SnO₂ and Fe₃O₄, etc semiconductor materials. From a mechanistic point of view, the mechanism responsible for photocatalytic oxidation can be explained as follows: (1) the semiconductor photocatalysts exposed to light with appropriate wavelengths can generate the couples of electron-hole; (2) these holes and electrons may either undesirably recombine liberating heat or migrate to the surface of the photocatalysts, where they can react with species adsorbed on the catalysts surface. (3) the holes with strongly oxidizing power can directly mineralize organic pollutants to CO₂, H₂O and inorganic salt, or react with H₂O to generate •OH_{abd}, while electrons can react with adsorbed molecular oxygen reducing it to superoxide radical anion which, in turn, reacts with H⁺ to form peroxide radicals.

When TiO₂ is irradiated by UV light with wavelengths <385nm, the reaction for photogeneration of couples of electron-hole is as follows:



The use of TiO₂ powder catalyst requires an additional treatment step to remove it from the treated effluents. Alternatively, the powder catalyst may be immobilized on suitable support matrices, thus eliminating the need for post-treatment removal. Jianwen et al⁽²⁵⁾ prepared TiO₂/ACF samples by immobilizing TiO₂ film on ACF and investigated photocatalytic degradations of methyl orange and acid fuchsine solution, respectively. The results showed that the dye compounds could be removed rapidly from water with the TiO₂/ACF samples because of the dual functions: absorption of ACF and photocatalytic degradation of TiO₂ film on ACF.

Generally, TiO₂ exposed to UV light with wavelengths of <385nm brings photocatalytic activity. The modification of TiO₂ by doping of metal and/or

nonmetal elements and the sensitization of TiO₂ with photosensitive materials can either enhance the photocatalytic activity or extend spectrum response range. Cui et al⁽²⁶⁾ prepared Fe-doped TiO₂ mesoporous layers on hollow glass microbeads and investigated its photodegradation of the methyl dye wastewater, suggesting that the doping of Fe ions makes the absorption edge of the TiO₂ red-shifted into the visible region, and the effective photodegradation of the methyl orange aqueous solution was achieved under visible light irradiation. Wang et al⁽²⁷⁾ fabricated N-doped TiO₂ and researched its photocatalytic degradation of phenol in aqueous N-doped TiO₂ suspensions with various light sources, proposing that photocatalytic activity of N-doped TiO₂ was markedly higher than that of pure TiO₂.

UV light, simulated solar light and visible light all can act as light sources for photocatalytic oxidation. From an economic point of view, photocatalysis is likely to benefit from the use of renewable energy sources to obtain power. In this direction, solar photocatalysis has gained considerable attention. However, nowadays, the main obstacle for application on a large scale of the technology is lower utilization efficiency of solar light. With overcoming these problems, photocatalytic oxidation will consequentially face a bright prospect.

2.3 Interactive Oxidation of Photoelectrocatalysis and Electro-Fenton

More recently, interactive oxidation which is a combination between photoelectrocatalysis and electro-Fenton has emerged⁽²⁸⁻³⁰⁾. TiO₂ semiconductor electrode is used as photoanode, and carbonaceous material electrode is used as cathode in an interactive reactor. The main advantages of interactive oxidation are: photoelectrocatalytic process and electro-Fenton process can occur simultaneously under force of UV light and direct current; organic pollutants are destroyed by the •OH_{abs} on photoanode surface and by the •OH in bulk solution. The mechanisms responsible for interactive oxidation are as follows⁽³¹⁾:

(1) the potential difference between photoanode and cathode can force electrons photo-generated in photoanode flowing to cathode, decreasing the recombination between electrons photo-generated and holes photo-generated and thus increasing quantum efficiency of incidence light;

(2) H_2O_2 electro-generated on cathode surface can directly decompose through reaction (8) to $\bullet OH$ under irradiation of UV light, increasing the concentration of $\bullet OH$ in solution;



(3) $Fe(OH)^{2+}$ generated in Fenton reaction can directly decompose through reaction (9) to Fe^{2+} and $\bullet OH$ under irradiation of UV light, increasing both the regeneration of Fe^{2+} and the concentration of $\bullet OH$ in wastewaters.



Generally, a TiO_2 semiconductor photoanode consists of conducting substrate such as titanium mesh, titanium sheet and conducting glass and TiO_2 film supported on the conducting substrate^(32, 33). Due to very strong oxidizing power and short life, $\bullet OH$ generated on the photoanode can not diffuse into bulk solution and thus can only oxidize the pollutants adsorbed on and close to the anode surface.

Because of the limited adsorbability of TiO_2 film supported titanium mesh, titanium sheet and conducting glass, pollutants in wastewater can not be enriched close to electrode surface, resulting in longer reaction period. Immobilization of TiO_2 film on activated carbon or activated carbon fiber to obtain TiO_2 -coated activated carbon or TiO_2 -coated activated carbon fiber, which, in turn, are used to fabricate photoanode, the reaction period can be shorten and oxidation efficiency can be increased^(34, 35).

3 Methods Based on Ozonation

Ozone is a sort of gas with special odor and lilac color. The density of ozone is 1.5 times higher than that of oxygen. The solubility in water is 10 times higher than that of oxygen. Ozone also is a strong oxidizing agent ($E^0=2.07V$) whose oxidizing power is stronger than oxygen, chlorine and permanganate, etc familiar oxidants. Ozone either decomposes in water to form hydroxyl radicals which are stronger oxidizing agents than ozone itself, thus inducing the so-called indirect oxidation or attacks directly certain functional groups of organic molecules. Ozonation has been traditionally employed in drinking water treatment for odor and taste control and disinfection, as well as for wastewater disinfection. Many authors reported that ozonation was useful for achieving total decolorization with partial degradation of some dyes in waters⁽³⁶⁻³⁹⁾. However, it is not quite effective for COD and BOD reduction. Lidia et al⁽³⁶⁾ reported a comparative study on oxidation of dispersed dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. Their study showed: ozonation gave excellent results of the removal of apparent color leading to complete decolorization in 1 min at the ozone dose of 50 mg/L, but the removal of COD was insufficient to reach the discharge standards; hypochlorite gave the worst results in terms of color and COD removal; electrochemical oxidation remove 90% of color and 39% of COD; the best treatment results were obtained with the Fenton process under the pH 3 and the hydrogen peroxide and ferrous sulphide doses of 600 and 550mg/L, respectively, with the final effluent fulfilling the requirements of discharge wastewater.

The main drawback of ozonation is the low solubility of ozone in water leading to its low utilization ratio during the treatment of wastewater. So the cost of ozonation needs to be further ascertained to enhance the competition of this method. In order to increase the treatment efficiency of ozonation, some combined treatment techniques based on ozonation, such as UV/O₃, H₂O₂/O₃, UV/ H₂O₂ /O₃ have been proposed in the literature. These combined treatment techniques have

proved effectual for the treatment of biorefractory organic pollutants⁽³⁶⁻³⁸⁾. UV/H₂O₂/O₃ can enhance the removal efficiency of volatile organic chloride, reaching the complete mineralization of the aromatic intermediates formed during the UV/H₂O₂/O₃ process⁽³⁹⁾. In addition, the development of ozone generator with the characteristics which are higher production efficiency and lower energy consumption also is one of key problems for the large-scale application of ozonation.

4 Methods based on ultrasonic sound

Ultrasonic wave is sound wave whose frequencies are higher than 20 kHz. Ultrasound irradiation or sonolysis is a relatively new technique in water treatment and, therefore, has unsurprisingly received less attention than other AOPs. Sonochemical reactions are induced upon high-intensity acoustic irradiation of liquids with ultrasonic wave at frequencies ranging from 20 to 1000 kHz. Ultrasonic irradiation can yield cavitations (microbubbles) in liquids. After taking in the diffused ultrasonic energy, these microbubbles will collapse instantaneously. At sites where microbubbles collapse, there will be above 2000 K temperature and over 50 kPa pressure with strong microjet and microstrike. Therefore, each microbubble acts as a small microreactor which produces different reactive species such as hydroxyl radicals, and heat. Three regions for the occurrence of ultrasonic degradation of organic pollutants are postulated: a hot gaseous nucleus where volatile organism would be oxidized into CO₂, H₂O and inorganics; an interfacial region with radial gradient in temperature and local radical density; and the bulk solution at ambient temperature where hydrophilic compounds such as azo dyes might be effectively destroyed by oxidative degradation, provided that sufficient quantities of hydroxyl radicals are ejected into the bulk solution during microbubble collapse. Although many studies reported the effective use of ultrasonic irradiation processes for the decolorization of various dye wastewaters, the overall

mineralization of these complex compounds is difficult to reach with ultrasound alone⁽⁴⁰⁻⁴³⁾. In addition, the cost of ultrasonic degradation is comparable to incineration based on economic analysis. Therefore, the combination of ultrasonic degradation with other AOPs has been considered as an effective method for treatment of biorefractory organic compounds in wastewater. Zhang's study⁽⁴⁴⁾ showed that the combination between ultrasound and advanced Fenton process could decolorize C.I. Acid Orange 7 more effectively. Miao et al⁽⁴⁵⁾ studied the degradation of phenol in water solution by an ultrasound-electrocatalysis system, suggesting that the total removal efficiency of phenol was higher than the sum of the removal efficiency in ultrasonic oxidation alone and the removal efficiency in electrocatalysis alone, with obvious synergetic effect.

Though ultrasonic degradation has been a brightly prospective technique for the treatment of wastewater, the technique is still at phase of experiment. Prior to the application of the technique to treatment of industrial wastewater, much works have to be conducted, such as the optimal design of ultrasound reactor and the quantitative characterization of reaction mechanism, etc.

5 Wet Air Oxidation (WAO)

WAO belongs to the family of AOPs and is a thermochemical process where hydroxyl radicals and other active oxygen species are formed. WAO can be divided into Sub-critical wet air oxidation (BCWAO) and supercritical water oxidation (SCWO)⁽⁴⁶⁾. BCWAO is conducted at elevated temperatures (i.e. 200~320°C) and pressures (i.e. 2~20 MPa). At temperatures and pressures above the critical point of water (374°C, 22 MPa), the process is referred to as supercritical water oxidation (SCWO) with its main feature being that gas and liquid phases form a homogeneous single phase. In this respect, organics and oxygen become completely miscible, thus eliminating mass transfer limitations which, in conjunction

with increased reaction temperatures, lead to very high reaction rates⁽⁴⁶⁻⁴⁷⁾. The capacity of WAO to transform recalcitrant compounds in a high strength of contaminated wastewater is the major reason for its development. Typically, WAO process has shown promising results (80~99% of COD removal) for a complete mineralization of organic compounds or for their degradation into a less complex structure, which is more biodegradable. Erdal et al⁽⁴⁸⁾ studied and compared the degradation of reactive black 5 azo dye in aqueous solution with UV/TiO₂, electro-Fenton and wet air oxidation, etc AOPs processes, found that wet air oxidation process was most effective method for decolorization and mineralization of the azo dye. In this process 77% of TOC removal was achieved at 250°C for 180 min treatment. Whenas, treatment of micro-pollutants by WAO is not an economically viable option as it would result in excessive specific energy consumption (i.e. energy per unit mass of pollutant destroyed). In addition, the rigorous reaction conditions (high temperature and pressure) of WAO which result in the complication of treatment device and high operating cost also restrict application of WAO.

6 Several Examples about Treatment of Biorefractory and Toxic Wastewater

One chemical plant in Yangzhou of Jiangsu province is a manufactory which produces professionally the intermediates used for pharmaceuticals. There are a large amount of organic pollutants such as nitrobenzene in production wastewater whose COD and chroma are 11240mg/L and 2000, respectively and pH is equal to 3. Through the pretreatment with Fenton's reagent-microelectrolysis technique and the final treatment with anaerobic filter cell-SBR process, the final effluent reaches the requirement of Chinese discharge wastewater (GB 8978-1996)⁽⁴⁹⁾.

One electron-hardware manufacturer of Guangdong province produces mainly

hardware. There are cyanide-loaded wastewater ($150\text{m}^3/\text{d}$), oil-loaded wastewater ($250\text{m}^3/\text{d}$), chromate-loaded wastewater ($250\text{m}^3/\text{d}$) and acid-alkali-loaded wastewater ($450\text{m}^3/\text{d}$) in production wastewater. The wastewater treatment plant of this factory can treat 1000m^3 of the production wastewater per day. After the treatment with a combined technology between oxidation-reduction and coagulation-precipitation, the final effluent reaches the requirement of discharge wastewater of Guangdong province (DB 4426-2001)⁽⁵⁰⁾.

One electroplating workshop in Chaohu of Anhui province fabricates professionally electroplated layer on surfaces of good-sized mechanical component. There are Cr^{6+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , CN^- , PO_4^{3-} etc ions in production wastewater. Total amount of the wastewater is $50\text{m}^3/\text{d}$; total concentration of the ions is about 300mg/L . Through the treatment with chemical oxidation followed by coagulation and precipitation, the final effluent fulfils the requirement of Chinese discharge wastewater (GB 8978-1996)⁽⁵⁰⁾.

7 The Conclusion

Along with the development of human society during late centuries, especially those advances by leaps and bounds in industry and scientific technology, environment has been affected severely. The satisfaction of people's material and spiritual demand also brings out some serious threaten to our living environment. Nowadays, environmental problem has become the discussion people all over the world need to join. As a new advanced wastewater treatment Process, AOPs has the merits of efficiency, general utilization and thoroughness. That is why AOPs has become the hotspot of research on the field of global wastewater treatment. Many scholars from all over the world have made outstanding contributions to this technical and have achieved remarkable development. Although the international co-operation has speed the progress of this research, AOPs still has its

disadvantage of high operation cost. To be applied on a large scale it still needs improvement. Therefore, the combination of advanced oxidation processes with traditional ways of wastewater treatment might become the tendency of this research in future. Besides that, it is significant to deepen the research on the reaction mechanism responsible for oxidizing toxic pollutants by AOPs. In order to obtain the best reactive condition of oxidizing organic pollutants and to find out the most persuading theory backing up the process of reaction, clearly, the elaboration of the reaction process and outcome in reactor would be essential. Also, research workers of each countries should reinforce the collaboration of technology transfer.

References

- (1) Fenton HJH. Oxidation of tartaric acid in the presence of iron. *J Chem Soc*, 1894, 65: 899-910.
- (2) Huang CP, Dong C, Tang Z. Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. *Waste Manage*, 1993, 13: 361-77.
- (3) Y K Kim, I R Huh. Enhancing biological treatability of landfill leachate by chemical oxidation. *Environmental Engineering Science*, 1997, 14(1): 73-79.
- (4) 肖羽堂, 许建华. 利用芬顿试剂预处理难降解的二硝基氯化苯废水. *重庆环境科学*, 1997, 19(6): 33-36. (Xiao Yutang, Xu Jianghua. Application of Fenton' Reagent in pretreating refractory dinitro-chlorobenzene wastewater. *Chongqing Environmental Science*. 1997, 19(6): 33-36.)
- (5) 李绍锋, 张秀忠, 张德明, 黄君礼. Fenton 试剂氧化降解活性染料的试验研究. *给水排水*, 2002, 28(3): 46-49. (Li Shaofeng, Zhang Xiuzhong, Zhang Deming, Huang Junli. Experiment on degradation of active dyestuffs by Fenton oxidation. *Water & Wastewater Engineering* . 2002, 28(3): 46-49.)
- (6) 张平凡, 王一平, 李微, 郭梨梨, 那永良. $H_2O_2-Fe^{2+}$ 氧化法处理对氨基酚工业废水的研究. *化学工业与工程*, 1999, 16(6): 330-334. (Zhang Pingfan, Wang Yiping, Li Wei, Guo Cuili, Na Yongliang. Treatment of waster from intermediate p -aminophenol manufacturing process with ferrous-hydrogen peroxide method. *Chemical industry and engineering*. 1999, 16(6): 330-334.)
- (7) Junshui Chen, Meichuan Liu, Jidong Zhang, Yuezhong Xian, Litong Jin. Electrochemical degradation of bromopyrogallol red in presence of cobalt ions. *Chemosphere*, 2003, 53: 1131-1136.
- (8) 刘梅川, 陈俊水, 鲜跃仲, 张莉, 徐继明, 金利通. 电生 $Co-H_2O_2$ 体系降解溴酚苯三酚红的研究. *化学传感器*, 2002, 22(2): 38-44. (Liu Meichuan, Chen Junshui, Xian Yuezhong, Zhang Li, Xu Jiming, Jin Litong. The Study of degradation of bromopyrogallol red by electro $Co_2+-H_2O_2$ system. *Chemical Sensors*. 2002, 22(2): 38-44.)
- (9) Hongzhu Ma, Xinhai Zhang, Qingliang Ma, Bo Wang. Electrochemical catalytic treatment of phenol wastewater. *Journal of Hazardous Materials*, 2009, 165: 475-480.

- (10) Anissa Dhaouadi, Lotfi Monser, Nafaa Adhoum. Anodic oxidation and electro-Fenton treatment of rotenone. *Electrochimica Acta*, 2009, 54: 4473-4480.
- (11) Chen J X, Zhu L ZH. Catalytic degradation of orange II by UV-Fenton with hydroxyl-Fe-pillared Bentonite in water. *Chemosphere*, 2006, 65(7): 1249-1255.
- (12) Feng J Y, Hu X J, Yue P L. Discoloration and mineralization of orange II by using a bentonite clay-based Fe nanocomposite film as a heterogeneous photo-Fenton catalyst. *Water Research*, 2005, 39(1): 89-96.
- (13) 盛义平, 李峥, 王秀丽, 甄丽敏. 新型高效气体扩散电极的制备与性能. *环境工程学报*, 2009, 3(6): 1084-1088. (Sheng Yiping, Li zheng, Wang Xiuli, Zhen Limin. Preparation and performance on a new kind of high effective gas diffusion electrode. *Chinese Journal of Environmental Engineering*. 2009, 3(6): 1084-1088.)
- (14) Enric Brillas, Birame Boye, Miguel Angel Banos, Juan Carlos Calpe, Jose Antonio Garrido. Electrochemical degradation of chlorophenoxy and chlorobenzoic herbicides in acidic aqueous medium by the peroxi-coagulation method. *Chemosphere*, 2003, 51: 227-235.
- (15) N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar. Decolorization of orange II by electrocoagulation method. *Separation and Purification Technology*, 2003, 31: 153-162.
- (16) Tahar N B, Savall A. Electrochemical degradation of phenol in aqueous solution on bismuth doped lead dioxide: a comparison of the activities of various electrode formulation. *J Appl Elect rochem*, 1999, 29: 277-283.
- (17) 周明华, 吴祖成, 汪大翥. 电化学高级氧化工艺降解有毒难生化有机废水. *化学反应工程与工艺*, 2001, 17(3): 132- 136. (Zhou Minghua, Wu Zucheng, Wang Dahui. Advanced Electrochemical oxidation processes for treatment of toxic and biorefractory organic wastewater. *Chemical Reaction Engineering and Technology*. 2001, 17(3): 132-136.)
- (18) A M Polcaro. Electrochemical degradation of 2-chlorophenol. *J Appl Electrochem*, 2000, 30(1): 146-151.
- (19) E Fokedey, A Van Lierde. Coupling of anodic and cathodic reactions for phenol electro-oxidation using three-dimensional electrodes. *Water Research*, 2002, 36(16): 4169-4175.
- (20) Agnieszka Kapałka, Gyrgy Foti, Christos Comninellis. The importance of electrode material in environmental electrochemistry, Formation and reactivity of free hydroxyl radicals on boron-doped diamond electrodes. *Electrochimica Acta*, 2009, 54: 2018-2023.
- (21) Panizza, M., Cerisola, G. Electrochemical degradation of gallic acid on a BDD anode. *Chemosphere* (2009), doi:10.1016/j.chemosphere.2009.09.007
- (22) Sires I, Centellas F, Garrido JA, Rodriguez RM, Arias C, Cabot PL, et al. Mineralization of clofibric acid by electrochemical advanced oxidation processes using a boron doped diamond anode and Fe^{2+} and UVA light as catalysts. *Appl Catal B Environ*, 2007b, 72: 373-81.
- (23) Fujishima A, Hondak. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 37 (1): 238 -245.
- (24) Frank SN, Bard AJ. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solution at TiO_2 powder. *J Am Chem Soc*, 1977, 99: 30-34.
- (25) Jianwen Shi, Jingtang Zheng, Peng Wu, Xiaojing Ji. Immobilization of TiO_2 films on activated carbon fiber and their photocatalytic degradation properties for dye compounds with different molecular size. *Catalysis Communications* 9, 2008, 1846-1850.
- (26) Lifeng Cui, Yuansheng Wang, Mutong Niu, Guoxin Chen, Yao Cheng. Synthesis and visible light photocatalysis of Fe-doped TiO_2 mesoporous layers deposited on hollow glass microbeads. *Journal of Solid State Chemistry*, 2009,182: 2785-2790.
- (27) Z. Wang, W. Cai, X. Hong, X. Zhao, F. Xu, C. Cai. Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO_2 suspensions with various light sources. *Appl. Catal. B: Environ*, 2005, 57: 223-231.

- (28) Y.B. Xie, X.Z. Li. Interactive oxidation of photoelectrocatalysis and electro-Fenton for azo dye degradation using TiO₂-Ti mesh and reticulated vitreous carbon electrodes. *Materials Chemistry and Physics*, 2006, 95:39-50.
- (29) Guoting Li, Jihui Qua, Xiwang Zhang, Huijuan Liu, Haining Liu, Electrochemically assisted photocatalytic degradation of orange II: Influence of initial pH values. *Journal of Molecular Catalysis A: Chemical*, 2006, 259: 238-244.
- (30) W.H. Leng, W.C. Zhu, J. Ni, Z. Zhang, J.Q. Zhang, C.N. Cao. Photoelectrocatalytic destruction of organics using TiO₂ as photoanode with simultaneous production of H₂O₂ at the cathode. *Applied Catalysis A: General*, 2006, 300: 24-35.
- (31) Yao-Hui Huang, Yi-Fong Huang, Po-Shun Chang, Chuh-Yung Chen. Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton. *Journal of Hazardous Materials*, 2008, 154: 655-662.
- (32) T.A. Egerton, M. Janus, A.W. Morawski. New TiO₂/C sol-gel electrodes for photoelectrocatalytic degradation of sodium oxalate. *Chemosphere*, 2006, 63: 1203-1208.
- (33) Zulkarnain Zainal, Chong Yong Lee, Mohd Zobir Hussein, Anuar Kassim, Nor Azah Yusof. Electrochemical-assisted photodegradation of mixed dye and textile effluents using TiO₂ thin films. *Hazardous Materials*, 2007, 146: 73-80.
- (34) Chunyong Zhang, Linjuan Gu, Yihua Lin, Yongxiang Wang, Degang Fu, Zhongze Gu. Degradation of X-3B dye by immobilized TiO₂ photocatalysis coupling anodic oxidation on BDD electrode. *Journal of Photochemistry and Photobiology A: Chemistry*, 2009, 207: 66-72.
- (35) Hou Y, et al, Electro-photocatalytic degradation of acid orange II using a novel TiO₂/ACF photoanode, *Sci Total Environ* (2009), doi:10.1016/j.scitotenv.2008.12.055
- (36) Lidia Szpyrkowicz, Claudia Juzzolino, Santosh Nkaul. A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Wat. Res.* 2001, 35(9): 2129-2136.
- (37) G Ohlenbusch, S Hesse, F H Frimmel. Effects of ozone treatment on the soil organic matter on contaminated sites. *Chemosphere*, 1998, 37(8): 1557-1569.
- (38) Nigel Graham, Wei Chu, Catherine Lau. Observations of 2,4,6-trichlorophenol degradation by ozone. *Chemosphere*, 2003, 51(4):237-243.
- (39) 雷乐成, 汪大翬. 水处理高级氧化技术. 第一版. 北京:化学工业出版社, 2001: 234-235. (Lei Yuecheng, Wang Dahui. *Water treatment advanced oxidation process. The first edition.* Beijing: Chemical industry publishing company. 2001: 234-235.)
- (40) Hoffmann M R, Hua I, Hocheimer M. Application of ultrasonic irradiation for the degradation of chemical contaminants in water. *Ultrasonic Sonochemistry*, 1996, (3): 163-172.
- (41) Kruus P, Burk R C, Entezari M H, et al. Sonication of aqueous solutions of chlorobenzene. *Ultrasonics Sonochemistry*, 1997, 4: 229-233.
- (42) Dewulf J, Langenhove H V, Visscher A D, et al. Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentrations: kinetics and modeling. *Ultrasonics Sonochemistry*, 2001, 8: 143-150.
- (43) Chunde Wu, Xinhui Liu, Dongbin Wei, et al. Photosono-Chemical degradation of phenol in water. *Water Research*, 2001, 35(16): 3927-3933.
- (44) Hui Zhang, Jianhua Zhang, Chunyang Zhang, Fang Liu, Daobin Zhang. Degradation of C.I. Acid Orange 7 by the advanced Fenton process in combination with ultrasonic irradiation. *Ultrasonics Sonochemistry*, 2009, 16: 325-330.
- (45) 缪娟, 符德学, 路兴杰. 超声协同-钛铁双阳极电化学降解废水中酚的研究. *煤炭学报*. 2005, 30(5): 652-655. (Miao Juan, Fu Dexue, Lu Xingjie. Degradation of phenol in wastewater by ultrasound/titanium-iron double-anodes electric catalysis oxidation system. *Journal of China Coal Society*. 2005, 30(5): 652-655.)
- (46) Maria Klavarioti, Dionissios Mantzavinos, Despo Kassinos. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environment*

- International, 2009, 35: 402-417.
- (47) Tonni Agustiono Kurniawan, Wai-hung Lo, G.Y.S. Chan. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. *Chemical Engineering Journal*. 2006, 125: 35-57.
- (48) Erdal Kusvuran, Sibel Irmak, H. Ibrahim Yavuz, Ali Samil, Oktay Erbatur. Comparison of the treatment methods efficiency for decolorization and mineralization of Reactive Black 5 azo dye. *Journal of Hazardous Materials B*, 2005, 119: 109-116.
- (49) 张键, 于林堂, 朱宜平, 吉祝美. 高浓度硝基苯类废水的处理. *中国给水排水*, 2006, 37(4): 57-59. (Zhang Jian, Yu Lintang, Zhu Yiping, Ji Zhumei. Treatment of high-concentration nitrobenzene-containing wastewater. *China Water & Wastewater*. 2006, 37(4): 57-59.)
- (50) 王广华, 隋军, 汪传新, 蔡桂琴. 氧化还原和混凝沉淀组合工艺处理电镀综合废水. *中国给水排水*, 2007, 23(20): 57-59. (Wang Guanghua, Sui Jun, Wang Chuan xin, Cai Guiqin. Treatment of electroplating synthetical wastewater by combined process of oxidation and reduction, coagulation and sedimentation. *China Water & Wastewater*. 2007, 23(20): 57-59.)
- (51) 袁守军, 郑正, 牟艳艳. 化学氧化-沉淀法处理电镀废水. *环境工程*, 2005, 23 (3): 22-24. (Yuan Shoujun, Zheng zheng, Mu yanyan. Treatment of electroplating wastewater by chemical oxidation-sedimentation process. *Environmental Engineering*. 2005, 23 (3): 22-24.)

提出年月日：2010年5月14日