The progress of catalytic technologies in water purification: A review

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Abstract

Catalytic technologies have been paid increasing attention in refractory pollutants abatement due to its practical and potential values in water purification. As effective and efficient approaches for water purification, Fenton's reagent, ozonation, electrochemical and photocatalytic methods have been widely studied and applied in different aspects and have been reviewed by several articles. In recent years, some novel catalytic processes based on above processes have been developed for enhancing the efficiency of removing the organics from water. This review emphasized on the recent development of heterogeneous catalytic ozonation, electrocatalysis in respect of novel electrodes and electro-Fenton method, photoelectrocatalysis process and photoelectron-Fenton in water purification. It was also an attempt to propose general ideas about mechanism and principle enhancing the catalytic efficiency for the degradation and the mineralization of organics in water.

Key words: catalytic technology; water purification; heterogeneous catalytic ozonation; electrocatalysis; electro-Fenton; photoelectrocatalysis; photoelectro-Fenton

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Introduction

The removal of hazardous substances from wastewater and remediation of contaminants in surface water, groundwater is a major problem in the world. Oxidation processes (biological, chemical or physical) are one of major steps during water treatment. Biological oxidation is considered to be economically feasible and widely applicable. Although, the presence of toxic pollutants in treated water might make the usage of this method impossible. Thermal destruction of chemicals at high temperatures, although effective, is not economically feasible. Chemical oxidation with the usage of several oxidants such as ozone, hydrogen peroxide, chlorine or chlorine dioxide generally overcomes these difficulties, although in many cases, it does not result in the total mineralization of water contaminants.

In recent years, catalytic technologies have been described as efficient means for the eliminating of organics pollutants. The technique generally use a combination of oxidation (O_3 , H_2O_2), irradiation, electron and catalyst as a means of generating hydroxyl radicals ($\cdot OH$), superoxide radicals ($O_2^{\cdot -}$) and hydroperoxyl ($HO_2\cdot$) radicals etc. at ambient temperature and pressure. The synergistic effect from various active species is much more powerful than individuals in enhancing the degradation and mineralization of refractory organic pollutants in water. The oxidative processes can enhance the mineralization efficiency, implying that the final products of degradation reactions are

carbon dioxide, short-chain organic acids, and inorganic ions, typically less toxic and amenable to biodegradation. The catalytic technologies predominantly include photocatalysis, electrochemical catalysis photo-electrochemical catalysis, catalytic ozonation, and so on. The application photocatalysis to water purification has been reviewed by several articles (Hoffmann *et al.*, 1995; Mills *et al.*, 1997). From the viewpoint of application to practical water treatment, heterogeneous catalytic ozonation, electrocatalysis, electron-Fenton, photoelectrocatalysis process, and photoelectron-Fenton will be presented in the following sections, concerning the synergistic effects of photo- and electro-catalysis, the catalytic materials and catalytic degradation process of contaminants.

1 Heterogeneous catalytic ozonation

Heterogeneous catalytic ozonation has received increasing attention in recent years due to its potentially higher effectiveness in the degradation and the mineralization of refractory organic pollutants and a lower negative effect on water quality. The major advantage of a heterogeneous over a homogeneous catalytic system is the ease of catalytic retrieval from the reaction media. It has been developed to overcome the limitations of ozonation processes, such as the formation of byproducts and the selective reactions of ozone, which are designed to enhance the production of $\cdot OH$. Co-based catalysts, such as Co/SiO_2 (Rakitskaya *et al.*, 1999), $CoOx/Al_2O_3$ (Konova *et al.*, 2006), have

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been used in ozone decomposition studies. In the case of $\text{CoOx}/\text{Al}_2\text{O}_3$ catalyst, the high oxidation activity in the presence of ozone has been ascribed to the high content of active and mobile oxygen which strongly depends on the preparation method. Gruttadauria *et al.* (2007) and Liotta *et al.* (2006) synthesized four series of cobalt-based catalysts, bare oxides Co_3O_4 and CoO , $\text{CoOx}-\text{CeO}_2$ mixed oxides, CoOx supported over alumina, and alumina-baria, and CoMgAl and CoNiAl hydrotalcites for the oxidative degradation of phenol in the presence of ozone. The CoNiAl material showed the highest activity, after 4 h of reaction the TOC removal was of 90%, however, a high amount of Ni^{2+} were also detected in solution (17 mg/L). Therefore, the attainment of active and stable catalysts for catalytic ozonation of organic pollutants in water is still a challenge.

Among recent research works on catalytic ozonation, some promising results obtained (Hu *et al.*, 2008; Xing *et al.*, 2008). Two series of catalysts, MnOx and CoOx supported over ordered mesoporous ZrO_2 (MZ) have been synthesized by wet impregnation, drying, water washing and calcinations with manganese acetate tetrahydrate as the metal precursor. XPS and ICP results showed that Mn and Co were highly dispersed into the pore channels and the surface of MZ. As reference, commercial ZrO_2 (CZ), which has nonporosity, smaller surface area and insufficient surface hydroxyls, was used as support. By the same method, little Mn and Co were loaded on the surface of CZ, and the dosages of Mn, Co were almost completely washed out with water in the step of water washing. These results suggested that the rich surface hydroxyl groups of MZ played an important role in the loading of MnOx , CoOx . These phenomena indicated that MnOx or CoOx was anchored on the surface of MZ by the interaction of $(\text{Mn}(\text{H}_2\text{O})_6)^{2+}$ or $(\text{Co}(\text{H}_2\text{O})_6)^{2+}$ with the surface hydroxyls of the support. In preparation, during impregnation and subsequent drying in air, the complex reacted with both the acidic and basic hydroxyls of MZ to form the linking $(\text{H}_2\text{O})_x\text{Mn}^{2+/3+}-\text{O}-\text{Zr}$ or $(\text{H}_2\text{O})_x\text{Co}^{2+/3+}-\text{O}-\text{Zr}$. Then, the excess Mn or Co, which was not connected directly to the surface of MZ, was almost completely washed out with water in the washing step. Thus, monolayer-dispersed MnOx or CoOx was formed by calcination. Therefore, the higher dispersions of MnOx and CoOx on MZ were attributed to the fixing role of surface hydroxyls and the diffusing role of water.

The catalytic activity of MnOx/MZ and CoOx/MZ was evaluated by the degradation of 2,4-D (2,4-dichlorophenoxyacetic acid) with ozone at pH 7 (Fig. 1). Obviously, more than 90% of total organic carbon (TOC) of 2,4-D were removed within 30 min in MnOx/MZIW and CoOx/MZIW suspensions with ozone. While 50% of TOC of 2,4-D were removed in MnOx/CZI suspensions with ozone. In contrast, only 28% of TOC for 2,4-D were removed at the same reaction time in the presence of ozone alone. The results verified that the multivalence oxidation states and the high dispersion of MnOx and CoOx enhanced the electron transfer, causing a higher catalytic reactivity. Also, more than 90% of TOC of

Fig. 1 The removal of TOC during the degradation of 2,4-D (10 mg/L) in aqueous dispersions of various catalysts with ozone. Conditions: pH 7; catalyst 1.5 g/L; gaseous ozone concentration 30 mg/L.

Ibuprofen was removed by the catalytic ozonation of MnOx/MZIW and CoOx/MZIW . By GC-MS analysis, the residue intermediates mainly were acetic acid, formic acid etc. aliphatic acid. The catalytic ozonation efficiency of these catalysts did not change greatly in the pH range 3.5–10.

Similarly, CuOx was highly dispersed on mesoporous $\gamma\text{-Al}_2\text{O}_3$ by an impregnation method with an aqueous solution of copper nitrate (Qu *et al.*, 2004). The catalyst exhibited high efficiency for the mineralization of alachlor. The removal rate of alachlor in TOC was more than 60% in $\text{CuOx}/\text{Al}_2\text{O}_3$ suspension with ozone while it was only 20% with ozone alone. Moreover, the studies of electron spin resonance and the effect of radical scavengers indicated that the more $\cdot\text{OH}$ radicals were resulted from the catalytic decomposition of ozone, inducing a higher effectiveness for the removal of refractory pollutants in water. The durable experiments of MnOx/MZ , CoOx/MZ and $\text{CuOx}/\text{Al}_2\text{O}_3$ revealed that these catalysts were stable and the concentration of the released metal ions from the catalyst was lower than 0.2 mg/L. These results suggest that catalytic ozonation with MnOx/MZ , CoOx/MZ and $\text{CuOx}/\text{Al}_2\text{O}_3$ is a promising technique for the mineralization of refractory organic compounds in water.

2 Electrocatalysis process

The electrochemical technology and its application in water purification have received world wide attention in the past decades, due to its advantages such as small reactor size, low land area demand, and easy to handle (Simonsson, 1997). The introduction of catalytic reaction into electrochemical technology, which is called as electrocatalytic technology, would not only notably increase the efficiency and decrease the cost, but also broaden its availability for the degradation of the recalcitrant pollutants (Rajeshwar *et al.*, 1994; Rodger and Bunce, 2001). In this article, we will focus on the review of the electrocatalytic oxidation in respect of high efficient electrodes and electro-Fenton method.

2.1 Electrocatalytic oxidation

The electrooxidation reactions mainly occur in the anodic compartment, which contributes to the conversion and/or the combustion of organic pollutants. Generally, the pollutants are degraded through the following two pathways: (1) the interactions between pollutants and anode, which is called direct oxidation; (2) the interactions between pollutants and oxidants (e.g., hydroxyl radicals, ozone, hydrogen peroxide, and hypochlorite) formed by the electrode reaction, which is called mediate oxidation. The catalysis during electrooxidation may be promoted through the modification and the adulteration of certain metal oxides (e.g., PbO_2 , MnO_2) on the surfaces of electrode. Additionally, the introduction of homogeneous and heterogeneous catalyzer into the reactor may also be valuable.

The improvement of the efficiency of electrochemical technique is of crucial importance for its application in practice. For example, various electrodes including Ti and Pt mesh (Boscoletto *et al.*, 1994), Pt/Ti (Tanaka *et al.*, 1999), SnO_2/Ti (Tanaka *et al.*, 2002), and carbon fiber (Kuramitz *et al.*, 2004) electrodes, have been evaluated for the electrochemical removal of Bisphenol A (BPA). However, Ti, Pt and Pt/Ti electrodes were not effective to achieve total mineralization of BPA due to electrode deactivation and poor generation of more hydroxyl radicals.

In the past several years, much effort has been devoted to the development of the electrodes with higher catalytic activity. Electrochemical properties of Polyoxometalates (POMs) have been intensively studied in recent years (Sadakane and Steckhan, 1998). An important reason is the ability of POMs anions to accept various numbers of electrons giving rise to mixed-valency species, which has made these compounds very attractive in electrode modification and electrocatalytic research (Sadakane and Steckhan, 1998). It is reported that POMs can be immobilized on ordered mesoporous carbon (OMC) to improve the catalytic activity (Lapkin *et al.*, 2003). It has already been established that POMs molecules can be firmly physically adsorbed to graphite materials (Schwegler *et al.*, 1992). This physical adsorption was an electrostatic attraction caused by proton transfer from POMs to graphite for modifying graphite materials with POMs (Schwegler *et al.*, 1992).

Additionally, the boron-doped diamond (Si/BDD) electrode also received great attention, and has been proved as successful anode material to destruct a variety of organic pollutants. It has many unique advantages and is largely generating the adsorbed hydroxyl radicals from water decomposition as shown in Eq. (1) (Murugananthan *et al.*, 2008).

PbO_2 calls the attention as an electrode material due to its easy and rapid preparation, besides being of low cost and quite stable in high-applied potentials in media of different pHs (Andrade *et al.*, 2008). Its electrocatalytic activity as well as its stability can be significantly improved

by the incorporation of doping ions, such as Fe^{3+} , Bi^{3+} , Co^{2+} , and F^- , into its crystalline matrix, acting as good dopants towards the oxygen transfer reaction, as well as ozone production.

In recent year, there were some progresses on the electrocatalytic oxidation. Wang *et al.* (2006a) investigated the electrochemical degradation of Acid Red B (ARB), with ACF as an anode or a cathode, respectively. The complete decoloration and the satisfactory mineralization of ARB was achieved under both conditions. Comparatively, the mineralization rate of ACF cathode system (70% TOC removal) was much higher than that of ACF anode system (30% TOC removal), owing to the much higher hydroxyl radical concentration in ACF cathode system.

Wang *et al.* (2006b) investigated the combined effects of electrooxidation and coagulation on the removal of pollutants (i.e., ARB) from solution. The pellets of manganese mineral in a fixed bed mode were arranged to two electrochemical compartments. In anode compartment, manganese mineral may catalyze the electrooxidation of organics, while in cathode compartment, the metal ions dissolved from minerals might form coagulate. The coagulant could flocculate and adsorb the organic pollutants. It was observed that the elimination rate of ARB remarkably increased when the electrolysis process was catalyzed by manganese mineral. After 480 min of treatment, the TOC removal percentage was 43.6%, while the removal percentages of the process using the manganese mineral alone and using the electrolysis alone were 9.3% and 20.8%, respectively, suggesting the catalytic effects of manganese minerals on the electro degradation of ARB.

2.2 Electro-Fenton process

The study of more efficient electrochemical methods for water purification based on the indirect electro-oxidation of contaminants involving electrogeneration of strong oxidants is also in progress. An increasing number of publications deal with the destruction of toxic and refractory organic pollutants in acid waters by electro-Fenton method (Brillas *et al.*, 1998, 2000; Panizza and Gerisola, 2001; Flox *et al.*, 2006; Irmak *et al.*, 2006; Xie and Li, 2006). The process based on the simultaneous electrogeneration of hydrogen peroxide from the two-electron reduction of O_2 on the cathode and the reduction of ferric ion to ferrous ion. The EF process consists of the following steps (Reactions (2)–(5)) (Oturán, 2000).

Carbon is widely used as a cathode material for H_2O_2 generation because it exhibits a wide range of electrochemical activity for H_2O_2 decomposition (Panizza and Gerisola, 2001). Activated carbon fiber (ACF) is a potential carbon material with characteristics of adsorption, conductivity and catalysis (Jia *et al.*, 1999). Because of its large surface area, ACF possesses high adsorption capacity.

Another benefit of ACF is that ACF felt promoted the electrogeneration of hydrogen peroxide from the two-electron reduction of O_2 on its surface, which favors the occurrence of electro-Fenton reactions if Fe^{2+} is additionally added (Droguet *et al.*, 2001).

Wang *et al.* (2005a) found that the H_2O_2 electrogeneration with ACF felt cathode (600 mmol/L) was much higher than that with graphite cathode (52 mmol/L) after 180 min of electrolysis, which contributed to the more significant TOC removal. The adsorption of AR14 onto ACF felt may be neglected, which led to a limit removal of about 6% after 360 min. The anodic oxidation, which employed RuO_2/Ti as anode, only contributed 19% to TOC removal. The employment of ACF felt as a cathode notably improved the degradation of AR14, which was further enhanced through the addition of 1 mmol/L Fe^{2+} and the occurrence of electro-Fenton reactions. The significant acceleration in the presence of Fe^{2+} could be ascribed to the existence of fast homogeneous reaction of organics with the great amounts of $\cdot OH$ generated, which non-selectively oxidize most organics remained in the system. Additionally, it was observed that the production of H_2O_2 may be promoted through the increase of current densities, therefore enhancing the degradation of organics. The Fe^{2+} dosage also significantly affected the degradation of AR14. An obvious increase of the rate of TOC decay was observed by adding Fe^{2+} . Raising initial Fe^{2+} concentrations from 0 to 1 mmol/L might result in an augmentation of TOC removal. However, the Fe^{2+} at higher concentrations exhibited adverse effects on TOC removal, due to the scavenging of $\cdot OH$ by Fe^{2+} .

The electro-Fenton reaction with an ACF felt cathode also promisingly contributed to the degradation of algae microcystins (MC-RR, MR-LR) (Wang *et al.*, 2005b). Quantitatively, 75% of MC-RR and 94% MC-LR were eliminated after 60 min electrolysis under the operation conditions of 6.6 mA/cm² current density, 1.0 mmol/L Fe^{2+} at pH 3. ACF not only increased the efficiency of O_2 utilization and the formation of H_2O_2 due to its high BET surface area, but also contributed to the adsorption and accumulation of microcystins, which was beneficial to microcystins degradation.

3 Photoelectrocatalysis process

Heterogeneous photocatalysis using semiconductor oxides, such as TiO_2 and WO_3 , has demonstrated to be very effective to treat pollutants in water (Ioannis and Triantafyllos, 2004; Balasubramanian *et al.*, 2004). Nevertheless, it encountered difficulties of separation and recovery when powder catalysts were used. However, for the fixation of TiO_2 , the most drawback is that the catalytic efficiency is too low to be used for the removal of pollutants. Furthermore, the high degree of recombination between photogenerated electrons and holes is sometimes a major limiting factor controlling photocatalytic efficiency (Vinodgopal *et al.*, 1993; Li *et al.*, 2000). Recently, the separation of photogenerated electrons and holes was proved to be accelerated by the application of an anodic bias to

TiO_2 film; and the lifetime of active holes and electrons was largely extended. As a result, the efficiency of photocatalysis was greatly enhanced (Ward and Bard, 1982). The rate of photocatalytic degradation of 4-chlorophenol increased greatly when the TiO_2 particulate film electrode was maintained at an external anodic bias (0.6 V versus SCE) (Vinodgopal *et al.*, 1993). Zlamal and his co-workers investigated the influence of an externally applied bias on the photocatalytic performance of self-organized TiO_2 nanotube layers. The nanotube layers were grown directly on Ti substrate by anodization of titanium in fluoride containing electrolytes and have different geometric dimensions. The photocatalytic activity of self-organized TiO_2 nanotube layers can significantly be increased by electrochemical bias (Zlamal *et al.*, 2007).

The main advantage of photoelectrocatalysis is its great versatility joined to the simplicity of the reactor in terms of construction and management. However, for the application at large scale, the main limitation is to find electrode materials with specific characteristics to make the process competitive. Ti/PbO_2 , Ti/SnO_2 , Ti/IrO_2 , glassy carbon are generally used (Augugliaro *et al.*, 2006). A series of TiO_2 -modified β - PbO_2 electrodes were prepared using co-deposition method and characterized by SEM and XRD (Li *et al.*, 2005, 2006a, 2006b). The results indicated that the modified β - PbO_2 electrodes were different from the unmodified ones. Compared with the unmodified one, the modified β - PbO_2 electrodes crystals became finer and the electrode became more compact and more uniform. The modified electrodes were used in electrochemically assisted photocatalytic degradation of dyes. In this process, a significant synergetic effect was observed between photocatalytic process and an externally applied electric field on the anode. Table 1 shows the kinetics parameters for different degradation methods (Li *et al.*, 2006a). The results showed that the degradation efficiencies were greatly enhanced when a potential across the electrodes (1.5 V) is applied. TiO_2 is scattered between PbO_2 crystals, and PbO_2 shows similar electrical conductivity to that of the metals, which is favorable in terms of electrocatalysis. Anodic bias potential provides a potential gradient within the photocatalyst layer to drive the electrons to the counter electrode along conductive PbO_2 crystals. This contributes to the inhibition of electron-hole recombination processes.

With an increase of TiO_2 amount used in codeposition solution, degradation efficiencies were improved to some extent for the modified β - PbO_2 electrodes. Photocatalytic efficiency was greatly enhanced by the application of

Table 1 Kinetics parameters for different degradation methods*

Degradation method	K_{app} ($\times 10^{-3} \text{ min}^{-1}$)	R
UV irradiation	1.31	0.99
Electrolysis	0.65	0.94
UV with disconnected electrodes	1.77	0.99
EAPD 1st time	3.84	0.93
EAPD 7th time	2.83	0.99
EAPD 1st time, $Ru_{0.3}Ti_{0.7}O_2$	1.06	0.95

* 1.5 V potential was applied across the electrodes when needed, at neutral pH (Li *et al.*, 2006a).

an external anodic bias when using Acid Orange 7 as model pollutant. The combination of photocatalysis and externally applied electric field was an effective way to improve the efficiency of photocatalytic process, which demonstrated its potential applicability in the process of photoelectrochemical decontamination for organic pollutants.

Anodic oxidation with boron-doped diamond (BDD) anodes is a new advanced oxidation process with many advantages as compared to other known electrode materials due to its low and stable background current, wide working potential window, and stable surface microstructure over a wide potential range (Wang and Farrell, 2004). The outstanding electrochemical properties of BDD recommend this material as an excellent substrate for electrocatalytic oxide layer in anode oxidation of organic contaminants (Chen *et al.*, 2003). The oxidation process at BDD anodes involves the production of $\cdot\text{OH}$ radicals scarcely adsorbed at the BDD surface: they consequently desorb and can attack the organic pollutant (Augugliaro *et al.*, 2006). Moreover, the BDD electrode exhibit p-type semiconductor properties. A novel configuration of hybrid electrode has been designated as photoelectrocatalytic diodes (PECD) by Qu and Zhao (2008). These contain nanoislands of n-type TiO_2 interfaced over a highly crystalline layered BDD electrode, yielding nanodimensional p-n junctions. This hybrid electrode exhibit high photoelectrocatalytic activities toward the degradation of Acid Orange II (AOII) and 2,4-dichlorophenol (2,4-DCP) due to the p-n effect and high electrocatalytic and photocatalytic activities of BDD electrode and TiO_2 particles. Atom force microscopy (Fig. 2) and scanning electron microscopy showed that the TiO_2 deposits consist of adherent nanomicro-sized particles, scattered on the BDD substrate. AOII and 2,4-DCP in a solution can be efficiently degraded at the hybrid electrode in the photoelectrocatalysis process. Some intermediates formed in electro-oxidation process such as phenols could not be detected in the photoelectrocatalysis process.

4 Photoelectro-Fenton process

Recently, there is increasing interest in the use of photoelectron-Fenton method for pollutant abatement (Boye 2003; Sirés, 2007; Skoumal *et al.*, 2008). The mineralization process can be accelerated by introduced UV light into electro-Fenton process. UV light can accelerate the mineralization process by: (1) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids, e.g., oxalic acid. That is, at acidic pH, oxalic acids behave as photo-active complexes in the presence of ferric ions which undergoes photo-decarboxylation reaction (Irmak *et al.*, 2006):

and (2) the regeneration of more Fe^{2+} from the additional photoreduction of Fe(OH)^{2+} , which is the predominant Fe^{3+} species in acid medium (Sires *et al.*, 2006):

The recent study of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), performed in an undivided cell with a Pt anode and an O_2 -diffusion cathode, showed that the photoelectrochemical process was more powerful than electro-Fenton process, which can yield only about 60%–65% of decontamination. The electro-Fenton method provides complete destruction of all reaction intermediates, except oxalic acid, which in the presence of Fe^{3+} forms stable complexes that remain in the solution. The fast photodecarboxylation of such Fe(III)-oxalate complexes by UV light explains the highest oxidative ability of the photoelectro-Fenton treatment, which allows the highest mineralization of highly concentrated acidic aqueous solutions of 2,4,5-T at low current and temperature (Brillas *et al.*, 2003).

The mineralization of an azo dye Acid Red 14 (AR14) by the photoelectro-Fenton process was studied recently by Wang *et al.* (2008). The process was studied in an undivided electrochemical reactor with a RuO_2/Ti anode and an

Fig. 2 Atom force microscopy images of BDD electrode (a) and BDD- TiO_2 hybrid electrode (b). Scale size 10.0 μm ; data scale 350 nm.

ACF cathode able to electrochemically generate H_2O_2 . Results indicate that the electro-Fenton process yielded about 60%–70% mineralization of AR14, while the photoelectro-Fenton could mineralize AR14 more effectively (more than 94% TOC removal) even at low current densities assisted with UV irradiation after 6 h electrolysis. The initial solution pH range 1.49–6.72 has little influence on the TOC removal because of the pH change during AR14 degradation in the photoelectro-Fenton process, which may be due to the formation of organic carboxylic acids such as oxalic acid. The ACF cathode showed a long-term stability during multiple experimental runs for the degradation of AR14, indicating its good potential for practical application in treating refractory organic pollutants in aqueous solutions.

5 Conclusions

The catalytic technologies have the great potential for water purification as demonstrated in the all above studies. At present, its application is mainly limited to laboratory or small scale use. However, due to these successful results, further investigation is to be carried out to handle some key problems, such as the development of novel catalytic materials, the visual light and the combination of different processes and so on. Especially, for the engineering application, more efforts are required to use available information on these tested catalytic process systems, which is mostly on a laboratory scale for the design of pilot-scale reactors applicable for the efficient treatment of industrial wastewater and drinking water.

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