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Degradation pathway of malachite green in a novel dual-tank photoelectrochemical catalytic reactor

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HIGHLIGHTS

- A novel dual-tank photoelectrochemical catalytic reactor was designed.
- Malachite green degraded in bipolar double-effect mode.
- Salt bridge replaced by a cation exchange membrane in the reactor.
- Degradation pathways of malachite green in the cathode and anode tanks were similar.

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ABSTRACT

A novel dual-tank photoelectrochemical catalytic reactor was designed to investigate the degradation pathway of malachite green. A thermally formed TiO_2/Ti thin film electrode was used as photoanode, graphite was used as cathode, and a saturated calomel electrode was employed as the reference electrode in the reactor. In the reactor, the anode and cathode tanks were connected by a cation exchange membrane. Results showed that the decolorization ratio of malachite green in the anode and cathode was 98.5 and 96.5% after 120 min, respectively. Malachite green in the two anode and cathode tanks was oxidized, achieving the bipolar double effect. Malachite green in both the anode and cathode tanks exhibited similar catalytic degradation pathways. The double bond of the malachite green molecule was attacked by strong oxidative hydroxyl radicals, after which the organic compound was degraded by the two pathways into 4,4-bis(dimethylamino) benzophenone, 4-(dimethylamino) benzophenone, 4-(dimethylamino) phenol, and other intermediate products. Eventually, malachite green was degraded into oxalic acid as a small molecular organic acid, which was degraded by processes such as demethylation, deamination, nitration, substitution, addition, and other reactions.

1. Introduction

Over the last few decades, as an advanced oxidation process, semiconductor photocatalytic oxidation has become one of the emerging technologies used for the elimination of organic pollutants because of the efficiency in its mineralization [1–3]. Photocatalytic oxidation can also oxidize organic pollutants to produce carbon dioxide, water and inorganic mineral ions as end products [4,5]. Different types of semiconductors have been used in generating highly reactive intermediates, primarily the hydroxyl radical ($^{\bullet}OH$), these semiconductors initiate a sequence of reactions leading to the partial or total destruction of organic pollutants such as chlorophenols and aromatic compounds [6,7].

Among the semiconductors used, pollutants treatment using TiO_2 photocatalyst (PC) has been demonstrated as a promising alternative to conventional water treatment because it can decompose and mineralize pollutant compounds in wastewater [3,8,9]. Unlike other semiconductors, TiO_2 is nontoxic, stable against photocorrosion, and inexpensive. For TiO_2 PC oxidation, the electrons in the semiconductor are excited from the valence band into the conduction band under UV irradiation, resulting in the generation of electron–hole pairs. The positive holes are powerful oxidants which can degrade organic compounds [10,11]. However, this type of PC system suffers from two typical defects [12,13]: the difficulty of separating TiO_2 particles from aqueous solutions when the photocatalytic reaction is carried out in an aqueous TiO_2 suspension system; and the low quantum yield due to the rapid recombination of photogenerated holes and electrons.

To solve these problems, many researchers have attempted to fix TiO_2 onto some carriers, such as glass and ceramics [14,15].

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However, the results showed that these immobilizing methods reduce photocatalytic activity. Numerous efforts have been made to improve the photocatalytic capability of TiO_2 film using various techniques including noble metal depositing, cation doping, non-metal doping, and semiconductor oxide coupling [16–18]. Nevertheless, TiO_2 PC oxidation efficiency could not be sufficiently promoted. Recently, photoelectrocatalytic (PEC) oxidation has been proven more efficient than PC oxidation because the photogenerated electrons at the TiO_2 anode are driven to a counter electrode via an external circuit [19–25]. The PEC process can prevent charge recombination and extends the lifetime of active holes. Subsequently, a number of studies demonstrated that PEC oxidation technology is more efficient than PC oxidation or electrocatalytic technology [26].

The traditional PEC method used in the wastewater treatment focuses mainly on anodic oxidation. The role of the cathode is usually disregarded and cannot be used to degrade pollutants [27]. However, when graphite electrode is used as a cathode, O_2 can be reduced to H_2O_2 at the graphite electrode under acidic conditions. In our previous work [28,29], we established a new PEC system that uses a graphite electrode as the cathode and TiO_2/Ti electrode as the photoanode. The anode and cathode tanks were connected by a salt bridge. In the cathode tank, $FeSO_4$ was added into the solution to establish a Fenton system with electrogenerated H_2O_2, so that the pollutants can be degraded in the cathode tank by Fenton's reagent. Compared with the efficiency of the conventional PEC system, that of the catalytic degradation in this new PEC system can be significantly improved. Despite this advantage, the dissolution of Fe^{3+} or Fe^{2+} in the cathode solution resulted in difficult analysis of intermediate products.

In a conventional PEC system, the pH in the anode solution decreases during the PEC process. On the basis of our previous work, we replaced the salt bridge with a cation exchange membrane. In the current work, the solution was irradiated by UV light. The cation exchange membrane allows for the transport of H^+ generated in the anode tank to the cathode tank, enabling the H_2O_2 production process to occur at the graphite electrode. The electrogenerated H_2O_2 was catalyzed by UV light, resulting in the H_2O_2/UV system for the catalytic degradation of pollutants in the cathode tank. Therefore, the efficiency of PEC degradation of pollutants could be enhanced.

Most of the previous publications on the degradation of organic compounds have mainly focused on the optimization of photoreaction conditions and the examination of the primary process by monitoring decolorization [30,31]. Less attention has been devoted to investigations on the degradation pathway of organic compounds. Therefore, determining which intermediates appear in the effluent and whether some long-life byproducts are generated during the PEC process is necessary. The intermediate products produced in the PEC process may be more toxic than parent compounds [32,33]. Especially, for disinfection byproducts (DBPs), large amount of information of DBPs regarding the reaction kinetics, pathways and by-product identification has been reported [34–39]. Najjar et al. [39] have identified an increase in toxicity was observed during chlorination suggesting that the first transformations products formed were more toxic than the parent compound, and four chlorination transformation products were detected by LC/UV/MS analysis. Moreover, the identified byproducts or intermediate products during the reaction can be used for the study mechanisms [40–43]. Fan et al. [40] investigated the BTX removal and byproducts formation on the basis of the combination of a plasma reactor energized by positive DC power supply and MnO_x/Al_2O_3 catalyst. Ma et al. [43] investigated degradation of microcystin-LR (MC-LR) in the presence of nitrous acid (HNO_2) under ultraviolet irradiation. The reaction intermediate products formed in the degradation process of MC-LR were identified by LC–MS, and the degradation pathways of MC-LR were proposed according to analysis of LC–MS. But studies on intermediate products and pathway of organic degradation process for both anode and cathode tanks are not still reported.

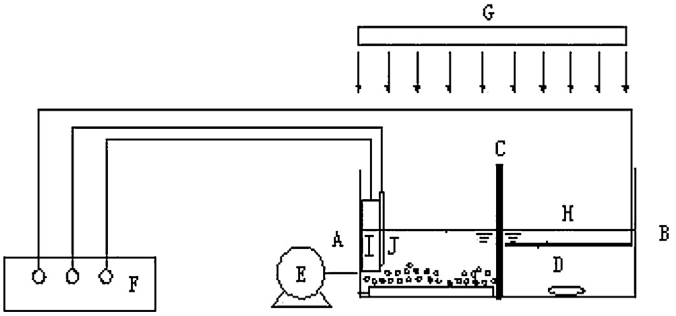

Fig. 1. Schematic of the photoelectrochemical catalytic reactor (A: cathode tank; B: anode tank; C: ionic exchange membrane; D: stirring bar; E: air pump; F: potentiostat; G: mercury lamp; H: working electrode; I: counter electrode; J: reference electrode).

In the present work, malachite green was employed as an indicator of the photoelectrolytic effect, malachite green is a biocide widely used in aquaculture to act as an ectoparasiticide. It is also used as a food additive and coloring agent [44]. Nevertheless, malachite green has become highly controversial due to the risks it poses to consumers of treated fish where it has been detected [45], since it intercalates with DNA causing carcinogenesis, mutagenesis and teratogenecity [46]. The effect of the PEC conditions on the efficiency of malachite green degradation in the bipolar double-effect model was investigated in detail. The structures and transformations of the intermediates retaining the chromophore group during the PEC process were identified by gas chromatography mass spectrometry (GC–MS) and Fourier transform infrared spectroscopy (FT-IR). Finally, the degradation pathway of malachite green in the bipolar double-effect mode was inferred.

2. Experimental

2.1. Materials and equipment

Malachite green ($C_{23}H_{25}N_2Cl$, MG, AR), anhydrous sodium sulfate (AR), sodium chloride (AR), and potassium bromide (spectroscopically pure) were purchased from Guangzhou Chemical Reagent Ltd. Methyl alcohol (chromatographically pure) was purchased from Germany. Titanium was purchased from Good fellow Cambridge Ltd. (purity, 99.6%), and used as raw material for the preparation of TiO_2/Ti electrodes. Other chemical reagents were purchased from Shanghai Chemical Reagent Ltd. A DJS-292 dual-display potentiostat was purchased from Shanghai Lei Ci Xin Jin Instrument Ltd. High-purity graphite, ACO-9610 oxygen pump, and UV high-voltage mercury lamp were purchased from Guangzhou Ltd. Type 217 saturated calomel electrode (SCE) and 85-1 magnetic stirrer were purchased from Shanghai Exact Science Instrument Ltd. A TU-1901 double-beam UV-visible spectrophotometer was purchased from Beijing. GC-MS-QP2010 and IR Prestige-21 were purchased from Shimadzu, in Japan.

2.2. Experimental setup and procedures

The novel dual-tank photoelectrochemical catalytic reactor is shown in Fig. 1. Malachite green degradation in aqueous solution was studied in the reactor using the TiO_2/Ti electrode as the photoanode, graphite electrode as the cathode, and the SCE as the reference electrode. The effective areas of the anode and cathode tanks were 19.6 and 12.3 cm^2, respectively. The cathode and anode tanks were connected by a cation exchange membrane. Both the