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Performance of nitrogen-doped graphene aerogel particle electrodes for electro-catalytic oxidation of simulated Bisphenol A wastewaters

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HIGHLIGHTS

- The new three-dimensional electrode system with the nitrogen-doped graphene aerogels particle electrodes is developed.
- The optimal technique parameters were explored.
- Simulated BPA waste waters are effectively degraded.
- Degradation pathway and intermediates are proposed.
- Three-dimensional electrode system shows good and stable removal performance.

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ABSTRACT

The treatment of effluent containing Bisphenol A (BPA) was investigated experimentally using nitrogen-doped graphene aerogel (NGAs) as particle electrodes in a three-dimensional electrode reactor for the electrochemical treatment was studied. The effects of the cell voltage, pH, the ratio of NGAs mass to solution volume and repeated times on the removal efficiency were investigated. Compared with commercial carbon particle electrodes, the NGAs exhibited stronger activity to remove BPA simulated wastewater. For 15 mg L^{-1} of BPA solution, the degradation rate of BPA exceeded 90% after treatment for only 30 min under the optimum conditions. The COD_{Cr} removal rate of BPA was 85%. Moreover, in the process of reused 50 times, the degradation rate of BPA can be kept in more than 85%. The COD_{Cr} removal rate was stable at about 73%. The intermediate products of electrochemical degradation of BPA were identified by liquid chromatography-mass spectrometry liquid chromatography (LC–MS), and a probable BPA degradation pathway was proposed. It was considered that •OH radicals by water electrolysis could constantly attack the aromatic ring to form various intermediates such as hydroxylated-BPA, isopropylphenol, hydroquinone, phenol and butantetraol, maleic acid, oxalic acid. These compounds were eventually mineralized by electrolysis into CO_2 and H_2O.

1. Introduction

In the current society, the economy has developed rapidly, and a wide variety of factories have been built to meet people's growing material needs. A complex composition of industrial waste water makes it increasingly difficult to handle. As environmental awareness has grown, traditional methods such as chemical precipitation and oxidation has been unable to meet the increasingly stringent requirements, so how to deal with the current complex industrial waste has become the world's environmental problems. Electrochemical treatment techniques generally do not need to add too many chemicals, but also because of it is simple, and take up space is small, also easy to manage, and then the amount of sludge near zero emissions, which many researchers called it clean water treatment technology [1–3].

Backhurst et al. [4] proposed the concept of three-dimensional electrode/triple electrode in the late 1960s, but until 70–80 s three-dimensional electrochemical reactor started striking and first applied in the analysis field, at a time when the three-phase fluidized bed and trickle bed department of gas–liquid–solid elec-

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trolyte are active. In the 90s, Brown, Comninellis, Szpyrkowicz et al. [5–7] began to explore the application of three-dimensional electrodes in water treatment, after the 21 st century Dai Zhang et al. [8–10] began a wide range of using three-dimensional electrode method to deal with sewage. Three-dimensional electrode compared with the traditional electrode (two-dimensional electrode) can be found that it adds many tiny microelectrodes in the electrolytic cell. The microelectrode is some granular or other fragments working electrode materials. Consequently, it can effectively increase the electrode area than in front of the body, and improve the capacity of unit tub. On account of the small distance between the particles, the migration distance of reactant is greatly reduced. This has satisfactory result of increasing the material mass transfer speed, improving current efficiency and treatment effect, degradation thoroughly, low energy consumption, high efficiency. In the form of loading microelectrode between traditional cell electrode and making the work surface charged is called a new pole (third pole), it can force all the electrochemical reaction on the surface of working electrode materials [4]. Compared to the two-dimensional electrode, three-dimensional electrode has many advantages, such as having a large specific surface area, greatly improved mass transfer of substances, high current efficiency, and large space-time yield [4,11]. However, if this technology is broad range of applications in wastewater treatment, it needs to resort to all sorts of measure to improve efficiency and manage circulation costs.

At present, the technology of three-dimensional electrode has been successfully applied to the processing of various pollutants. There are a large number of research articles on the application of this technology to eliminate organic pollutants, such as phenol [12,13], anionic surfactants [14], acid orange 7 [15], from wastewater in the recent years. In this experiment, Bisphenol A (BPA), an environmentally harmful, low toxicity chemicals, recalcitrant, organic pollutant with high biological activity was used as a research subject.

Recent studies have been focused mainly on developing the new type of particle electrodes. Activated carbons were widely used as the particle-electrodes for a long period of time. Carbon aerogels (CAs) are novel mesoporous carbon materials with a three-dimensional net structure of the only aerogel with electrical conductivity. Due to their unique physicochemical characteristics, such as high specific surface area and porosity, excellent chemical stability, and high conductivity, CAs have proved to be promising materials for use in adsorbents, catalyst supports, super capacitors so on several aspects [16]. Guifen Lv et al. [12] had succeeded in using CAs as particle electrodes to treat phenol wastewater. They discussed the effect of microelectrode type in the process of electrochemical oxidation of phenol. It was proved that CAs was potential material of a third electrode from both aspects of specific energy consumption and the removal efficiency. Graphene aerogels (GAs) with the exception a series of properties of CAs, in particular, on the electrical conductivity, GAs conductivity is about 10 S/m–10^2 S/m [17]. However, CAs is less than 10 S/m. That is believed this advantage would be helpful the application of GAs in the three-dimensional electrodes. In recent years, the researchers studied the modification of GAs in order to achieve its outstanding performance can expand its actual application in various fields such as adsorbent, electrochemical, energy storage. Doping graphene with other chemical elements has been extensively applied to the modification it which can tailor the band structure, and modulate electronic properties open the band gap in graphene [18]. Nitrogen is considered to be an excellent element for the chemical doping of graphite because it is of comparable atomic size and contains five valence electrons available to form strong valence bonds with carbon atoms [19]. Song et al. [20] proposed that "incorporating heteroatoms such as nitrogen into graphene can improve and modulate its physicochemical characteristics, especially its electrochemical performance." Accordingly, it is believed that the nitrogen-doped graphene aerogels (NGAs) electrical conductivity and catalysis characteristics is stronger than GAs [21]. To our knowledge, this is the first report of graphene aerogels as particle electrodes remove pollutants from water for the three-dimensional electrodes.

Sun et al. [22] used Ti-Sn/γ-Al_2O_3 as particle electrodes to treat chloramphenicol (CAP), and concluded that more than 70% of CAP was degraded under the optimal conditions. Li et al. [23] investigated the degradation of 2-diethylamino-6-methyl-4-hydroxypyrimidine (DTMHP) using three-dimensional electrodes reactor with ceramic particle electrodes. They found that the maximum degradation efficiency was 83.45% for pyrimidine ring and 35.17% for COD within 150 min under initial pH of 3 and cell voltage of 15 V. Despite many researches devoted to the three-dimensional electrode system, few studies on the use the system for BPA treatment have been reported. However, some studies have investigated the degradation of BPA by two-dimensional electrodes technology. Examples include investigations on the effect of anodes (Pt [24], boron-doped diamond and modified SnO_2-Sb [25,26]) on BPA removal. He et al. [27] used a CNT-covered polyester yarn electrode to remove of BPA. Through electrochemical polymerization and degradation on this electrode, high removal efficiency of BPA was obtained, at levels as high as 8.1×10^{-5} mol/g with 0.75 V applied potential. One of the purposes of this study was to assess the effectiveness of a novel three-dimensional electrodes system in degrading BPA. The comparison between the existing methods and the three-dimensional electrode system with NGAs as particle electrodes is shown in Table S1.

To utilize the excellent electrical conductivity and high specific surface area of graphene aerogels for water treatment uses, the NGAs were prepared and used as particle electrodes for anode cell. After power up, the particle electrode is polarized quickly, and the formation of numerous small working electrodes. The high specific surface area of NGAs provides more active sites for BPA, which is enriched to the surface of the polarized particle electrode, so as to achieve rapid and effective removal. The removal efficiency of NGAs was compared with that of the commercial carbon particle electrode. The optimal technique parameters for such a new treatment system were explored. Furthermore, the intermediate products and the possible reaction pathway in the degradation of BPA by the three-dimensional electrode system were also analyzed.

2. Materials and methods

2.1. Materials

Commercial wastewater treatment active carbons (ACs) and powder-like graphite (purity ≥99.99%, Sinopharm Chemical Reagent Co., China) was used in experiments. Bisphenol A (reagent grade ≥99%) was formed Shanghai Chemical Reagent Factory. All other chemicals used were analytical reagent grade and used as received without further purification. All solutions were prepared with deionized water.

2.2. Preparation of samples

Graphene oxide (GO) samples were synthesized from powder-like graphite by using the Hummers method, as reported elsewhere [28–30]. The NGAs were prepared by the hydrothermal synthesis method [31,32], from GO samples.

The NGAs were prepared by using the following procedure, in which ethylenediamine (EDA) aqueous solution was used as the reducing agent and the nitrogen source in the. In a typical procedure, EDA (80 μL) was slowly added to the GO suspension (20 mL)