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Short Communication

Dynamic model of organic pollutant degradation in three dimensional packed bed electrode reactor

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HIGHLIGHTS

- A three-stage organic degradation dynamics model was deduced.
- Dynamics model relies on the mass transfer coefficient and limit current density.
- The experiments verify that the kinetics of organic degradation is not a simple first-order.

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ABSTRACT

A dynamic model of semi-batch three-dimensional electrode reactor was established based on the limiting current density, Faraday's law, mass balance and a series of assumptions. Semi-batch experiments of phenol degradation were carried out in a three-dimensional electrode reactor packed with activated carbon under different conditions to verify the model. The factors such as the current density, the electrolyte concentration, the initial pH value, the flow rate of organic and the initial organic concentration were examined to know about the pollutant degradation in the three-dimensional electrode reactor. The various concentrations and logarithm of concentration of phenol with time were compared with the dynamic model. It was shown that the calculated data were in good agreement with experimental data in most cases.

1. Introduction

Most of the organic pollutants, such as pharmaceuticals, dyes, and daily chemicals not only aggravate environment, but also do harm to human health. Because of the complicated structures, they are toxic and non-biodegradable. Phenol, which is a typical organic compound widely used as intermediate in the synthesis of plastics, colors, pesticides, and insecticides, has an unpleasant odor, and poisons to human (Dąbrowski et al., 2005). It can lead to fish death, even if the concentration of phenol in water is low. However, it is very difficult to reach wastewater discharge standards only by employing traditional biological methods for the degradation of chemical wastewater. Advanced oxidation processes (AOP), such as heterogeneous and homogeneous photocatalysis, ultraviolet or solar visible irradiation, electrolysis, ozonation, ultrasound and wet air oxidation (Shannon et al., 2008), have received more attention for its ability to effective degradation of persistent organic wastewater recently. Electrochemical oxidation is a significant kind of AOP processes, because it has strong oxidation ability, high efficiency and no requirement for chemical reagents and temperature (Martínez-Huitle and Ferro, 2006; Comninellis et al., 2008; Berenguer et al., 2009; Oller et al., 2011). For electrochemical oxidation, the main equipment is a electrode reactor. The traditional two-dimensional reactor has such defects as low space-time ratio and current efficiency. The three-dimensional reactor can increase the number of active sites and decrease the mass transfer distance by adding the third electrode (Fockedey and Van Lierde, 2002; Zhao et al., 2010; Zhang et al., 2013), which enhances the efficiency of the reactor greatly.

Generally, the third electrode is mainly composed of activated carbon, metal particles, or metal oxides. With unsaturated bonds, activated carbon has crystalline defects in its structure, which

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makes it as an ideal catalyst in the oxidation-deoxidation reaction (Pandolfo and Hollenkamp, 2006). Additionally activated carbon can be used as a carrier to support metal oxides as well, for its high specific surface area, rich pore structure and strong adsorption capacity (Yenisoy-Karakaş et al., 2004). Therefore, activated carbon has become the most popular particular electrode. In a three-dimensional electrode reactor, activated carbon polarized by the external electric field can form numerous microelectrodes in the whole system, and improve the efficiency of electro-catalytic degradation greatly (Can et al., 2014). The three-dimensional electrode reactor has been widely applied in the treatment of organic wastewater, such as phenols, dyes, oils, surfactants, nitrates, and so on. Xiong and Karlsson, 2002 used activated carbon as the third electrode to investigate the degradation of oxalic acid wastewater under the conditions of 30.0 V cell voltage and 7.0 L min^{-1} airflow and achieved a COD removal efficiency over 90% after 60 min degradation (Xiong and Karlsson, 2002). Kong et al. (2006) reported that the COD removal efficiency of 86% could be achieved for sodium dodecyl benzene sulfonate using modified kaolin as the third electrode and Ti/Co/SnO_2–Sb_2O_3 as the anode (Kong et al., 2006). Zhou and Lei, 2006 removed p-nitrophenol at the initial concentration of 150 mg L^{-1} in an activated carbon three-dimensional electrode reactor. The results showed that p-nitrophenol could be removed completely after 30 min electrolusis. The removal efficiency did not decrease significantly after five times running. It has been proved that the activated carbon had the ability of partial electrochemical regeneration and the production of hydroxyl radicals during the electrolysis process (Zhou and Lei, 2006). Li et al. (2016) applied three-dimensional electrode reactor to gas disposal. Firstly, activated carbon was coated with high-ionic strength solution, then CH_3Br in the gas phase was captured and electrolyzed on it. The debromination rate could reach 96% for 15 h reaction, and the system could run stably for more than 50 cycles (Li et al., 2016).

In recent decades, the study on the three-dimensional electrode reactor is mainly focused on the third electrode and the optimal operation parameters to achieve maximum organic removal rate for different organic pollutants. The operation of the three-dimensional electrode reactor is complicated, which not only relates to the degradation of organic species, electrodes materials, electrolyte, but also involves adsorption (Zhou and Lei, 2006), electric adsorption (Ban. et al., 1998) and electrocoagulation (Mollah et al., 2004). At present, a few researchers focus on the dynamics of the three-dimensional electrode reactor.

In this work, three-stage degradation kinetic equations were proposed based on mass balance, Faraday's law, the limiting current density, and a series of assumptions. To verify the model, phenol was used as the model compound to investigate the degradation of pollutants in an activated carbon fixed bed three-dimensional electrode reactor. The parameters such as current density, initial concentration of electrolyte, initial pH, volume rate of flow, and initial concentration of phenol were investigated. The experimental data of phenol concentration and logarithm of phenol concentration were matched using the three-stage degradation process equations.

2. Experiment

2.1. Material and experimental equipment

Deionized water was used to prepare the simulated phenol wastewater solution. Anhydrous sodium sulfate was used as an electrolyte, and sodium hydroxide and concentrated sulfuric acid were used to regulate the pH of the initial effluent of phenol. Methanol and ultrapure water were used as the mobile phase in high performance liquid chromatography. All reagents were purchased from Tianjin Kemiou Chemical Reagent Company. All the reagents were analytically pure except for methanol, which was chromatographically pure. The activated carbon used as the third electrode was obtained from Ningxia Huahui Activated Carbon Company, and had an average particle size of about 2–3 mm and a specific surface area of approximately 850 $m^2 g^{-1}$ determined by the BET method.

A semi-batch reactor, as shown in Fig. 1, was made of polymethyl methacrylate. The anode material was Ti coated with iridium oxide and ruthenium oxide (from Suzhou Titanium Electrode Manufacturing Plant), and the cathode was a graphite plate (from Beijing Jinglong Carbon Graphite Company). The two electrode plates with dimensions of 30 mm × 120 mm × 1 mm were placed vertically and parallel to each other. The reaction area was 30 mm × 20 mm × 100 mm, and the effective volume of the reactor was about 60 mL. A microporous plate made of polytetrafluoroethylene with 1 mm round holes distributed uniformly was fixed at the bottom of the reactor. Activated carbon with adsorptive saturation was packed directly into the reactor up to the outlet. A DC power supply of type KXN-305D (Zhaoxin Company) was used, and the adjustable current range was 0–10 A, and the voltage range was 0–30 V.

2.2. Experimental procedure

2.2.1. Pretreatment of activated carbon

A certain amount of activated carbon was washed with deionized water, cleaned with an ultrasonic cleaner for 30 min, washed with deionized water for 5–6 times, and finally dried in 105 °C for 24 h.

2.2.2. Electrolysis experiment

The activated carbon was saturated by adsorption of 100 mg L^{-1} phenol. Using the single factor variable method, the effects of current density, concentration of sodium sulfate electrolyte, pH value, flow rate and initial phenol concentration on the reaction were investigated. With an increase of temperature, the rate of electrochemical reaction does not increase significantly and the corrosion of electrode is accelerated. Therefore, in this study, the effect of temperature on the reaction was neglected and all experiments were carried out at room temperature.

The flow rate of the reactor is decreased in order to enhance conversion, which will result in the accumulation of reaction product and reaction heat. The recycle plug flow reactor employed in this research can solve this problem and it is convenient for

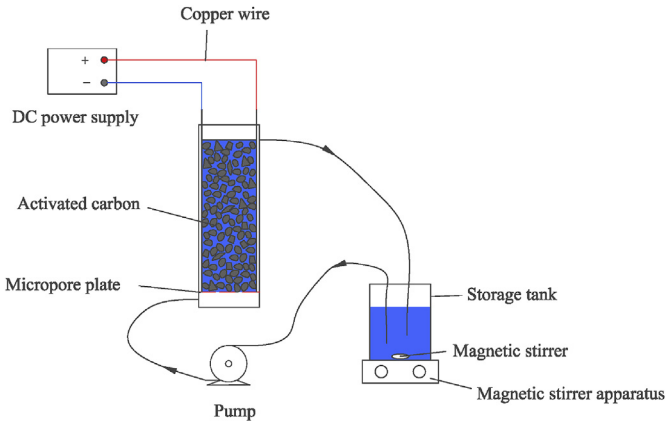

Fig. 1. Experimental set-up of a semi-batch reactor.