



Electrochemical degradation of phenol by in situ electro-generated and electro-activated hydrogen peroxide using an improved gas diffusion cathode



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ABSTRACT

Electro-Fenton process represents an attractive and effective technology in destroying hazardous and organic pollutants. However, the low H₂O₂ productivity and the narrow working pH range have been limiting its further industrial application. In this study, an improved gas diffusion electrode constructed by carbon black and PTFE was designed to improve H₂O₂ productivity. The diaphragm electrolytic device was then used to degrade phenol without adding any catalyst. Results showed that the maximum concentration of H₂O₂ was 275.5 mM, which was roughly eight times higher than the value obtained by traditional reference cathode. The effects of the operation parameters, such as current density, supporting electrolyte, pH, air flow rate, and phenol concentration, on phenol removal were systematically optimized. Under the optimum conditions, phenol removal reached almost 100% after 40 min and the mineralization efficiency in terms of TOC exceeded 85% after 120 min. Experiments indicated that the degradation of phenol in the electrochemical process was dominated by radical based mechanisms, which was obtained by the electro-generation and the subsequent electro-activation of H₂O₂ at the cathode interface. It is suggested that the electro-activated H₂O₂ process with less influence of pH and ferrous is a potential method for the electrochemical degradation process.

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1. Introduction

Electrochemical advanced oxidation processes (EAOPs) are considered environmentally friendly emerging alternatives for the elimination of contaminant caused by a multitude of organic micro pollutants in wastewaters [1]. Electro-Fenton process, as proposed by Brillas et al. [2], is one of the most widely used EAOPs to control pollution through redox reactions involving either direct oxidation on the electrode surface, or synergistic systems based on an oxidant species generated in situ. In this process, hydrogen peroxide (H₂O₂) is electro-generated by the two electron reduction of oxygen on cathodes surface, while Fe²⁺ is added form outside and continuously regenerated at the cathode [3] or provided form sacrificial cast iron anodes [4].



Although the electro-Fenton reaction has been widely considered for the degradation of polluted waters, it has some drawbacks for practical applications in wastewater treatment, i.e., the low ratio of H₂O₂ productivity and the narrow working pH range [5]. Furthermore, pH adjustments and Fe²⁺ addition, i.e., acidification and neutralization before and after treatment, are a complicated implementation process and require operating costs [6]. Therefore, more efficient electrochemical methods on the electro-degradation of organic pollutant are now under way.

In the electro-Fenton process, the optimum pH varies from 2 to 4, since it is essential for iron species [7]. Iron species start to precipitate as ferric hydroxides at higher pH values [8]. Conversely,

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iron species develop stable complexes with H_2O_2 at lower pH values, leading to deactivation of catalysts [4]. As a consequence, the optimum pH value is the disadvantage of electro-Fenton process, since the pH of most wastewater is not within the optimal range [4]. Besides, iron ions may be removed from wastewaters by adding alkaline chemicals after the treatment of electro-Fenton oxidation, leading to the generation of chemical sludge [9]. The burden resulted from the sludge treatment is another important shortcoming of the Fenton process.

Recently, it has been declared that $\bullet\text{OH}$ and sulfate radical ($\text{SO}_4^{\bullet-}$) could be generated via electrolytic activation of H_2O_2 [10,11] and persulfate anions [12–14], respectively. Furthermore, H_2O_2 or persulfate anions may be in situ electro-generated by the electrolytic process [11,12]. The electro-activated persulfate anions have been used to dispose aniline [15], dinitrotoluenes [13], 2,4,5-trichlorophenoxyacetic acid [12], wherein the main oxidizing agent is supposed to be $\text{SO}_4^{\bullet-}$, shown as Eq. (5). Similarly, Wang et al. [11] developed a C/PTFE gas-diffusion cathode to improve the H_2O_2 productivity, and used it to degrade the aqueous organic pollutant without adding metal catalyst. It has been demonstrated that the decomposition of H_2O_2 in the warm alkaline solution can produce the highly reactive $\bullet\text{OH}$ (Eq. (6)) during electrolytic process [11,16]. Therefore, it is rational to hypothesize that the electrolytic process can simultaneously catalyze the production of H_2O_2 by the oxygen reduction reaction as well as the decomposition of H_2O_2 to $\bullet\text{OH}$ by the electron transfer reaction.



Theoretically the performance of the effective destruction of pollutants in the indirect electro-oxidation system, i.e., electro-Fenton, substantially depends on the H_2O_2 productivity, thus an ideal cathode with highly production of H_2O_2 is vital and becomes one major concern in this area [17]. Actually, gas diffusion electrodes (GDE) provide an alternative type of electrode to improve H_2O_2 productivity, because it possess porous structures with hydrophobic characteristics that allow unlimited supplies of oxygen to be delivered to the electrode/electrolyte interface [18]. The design of a GDE allowed an unlimited supply of gaseous reagents to pass through the porous structure to the electrode/electrolyte interface, thus avoiding mass transport limitation of the reaction [17,19–21]. So far, various reports are available concerning the use of GDE for in-situ electrosynthesis of H_2O_2 . Those reports of the GDE were mainly focused on various carbon-based materials, and its different modifiers, which have investigated with regard to the oxygen reduction reaction (ORR) with the purpose of achieving

higher currents at less negative potentials [22]. However, the effects of the cathodes construction were usually neglected. The effective conduction of proton/electron and access of reactant gas depended on the cathode structure [23]. The design of the gas diffusion layer was also imperative to the gas transfer and waterproof management, while the catalyst layer was crucial to ORR kinetics and three-phase interfaces [16]. Consequently, a well-designed catalyst layer improved the uniform gas diffusion and favored the reaction process [7,23]. In our previous study, we have confirmed that the improved GDE was an efficient cathode for H_2O_2 production [24]. This paper presents our research on the preparation of the improved GDE, and then used to treat the aqueous organic pollutant without adding metal catalyst. The effects of some critical reaction parameters such as initial pH, current density, air flow rate and phenol concentration on the phenol removal were investigated. Degradation mechanism of the electrolytic process was also proposed.

2. Experimental

2.1. Materials

The carbon black powder (CB, Vulcan XC 72R) was purchased from Cabot Corporation and used without any further treatment. The nitrogen adsorption isotherm and the particle size distribution of the CB samples are presented in Fig. S1. Polytetrafluoroethylene (PTFE, 60 wt%, Hesen, China) was used as binder. Nafion-117 used as the cation exchange membrane was purchased from Dupont (New York, USA).

2.2. Preparation procedures of the improved GDE

The improved GDE consisted of a titanium meshes and a conductive catalytic layer (CCL). Different from traditional GDE which comprise by gas diffusion layer and catalyst layer [16,25], the CCL simultaneously acted as gas diffusion layer and catalyst layer. After being hydrophobic treated by PTFE (60 wt%), the titanium mesh was used as the matrix.

The fabrication procedure was in accordance with the method described by Luo et al. [24]. The flow diagram is briefly presented in Fig. S2. CB powder of 2.0 g was distributed into an appropriate amount of ethanol and ultrasonic agitated for 20 min in a beaker, followed by dripping 60 wt% PTFE suspensions of 0.83 g (CB: PTFE = 4: 1) into the blend slowly. After stirred uniformly, the mix was still operated with ultrasonic agitation to disperse the carbon black and the PTFE to form fine networks of gas channels. The blend was stirred and the redundant ethanol was removed to obtain a paste. The paste was just rolled on the either side of the

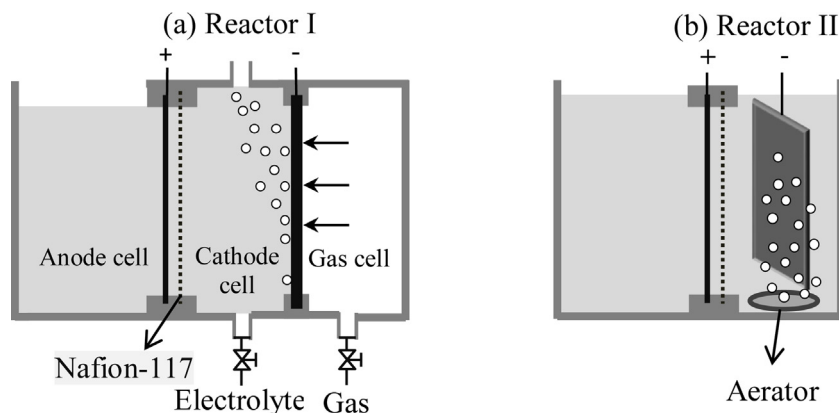


Fig. 1. Schematic diagram of the two reactor.

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