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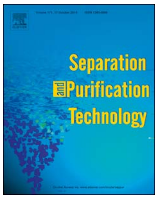

Short Communication

A novel bio-electro-Fenton process with $FeVO_4$/CF cathode on advanced treatment of coal gasification wastewater

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A B S T R A C T

An investigation was carried out aimed at checking the feasibility of the novel bio-electro-Fenton process with $FeVO_4$/CF cathode on advanced treatment of coal gasification wastewater. The maximum power density arrived 849.7 mW/m^3 in MFC-$FeVO_4$/CF system, which was corresponding to a current density of 2.6 A/m^3 at the voltage of 326.8 mV. The concentration of BOD_5, COD, TOC and total phenols in the cathode effluent under short-circuit conditions were 4.5 mg/L, 32.5 mg/L, 8.8 mg/L and 15.6 mg/L, respectively, which all met the class-I criteria of the Integrated Wastewater Discharge Standard. $FeVO_4$/CF could be employed as a two-way Fenton-like catalyst that leads to the production of more reactive oxygen species. The in situ generation of Fenton-like reagents (Fe(II, V(IV) and H_2O_2) at the cathode was demonstrated by the cyclic voltammetry measurement. This novel process provides a cost-effective alternative to extend the practical merits of traditional MFCs and Fenton towards advanced treatment of industrial wastewater.

1. Introduction

The coal gasification wastewater (CGW) generated in coal gas purification and condensing operation contains a large number of toxic and refractory compounds, characterized by the extremely low biodegradability [20]. The treated effluents in most of biological processes were not able to comply with the increasingly stringent environmental regulations [9]. Hitherto, more efforts are essential to be focused on advanced treatment of biologically pretreated CGW.

Advanced oxidation processes (AOPs) have been considered as potentially powerful methods and have drawn growing interests in the industrial wastewater treatment, aiming at the removal of the recalcitrant organics [12]. As one of AOPs, Fenton reactions, based on the reaction of hydrogen peroxide (H_2O_2) with ferrous ion (Fe^{2+}) to generate hydroxyl radicals ($^{\cdot}OH$), has proven to be one of the most effective methods to degrade recalcitrant organic pollutants in wastewater. Previous studies have demonstrated that Fenton reactions are effective in degrading many organic pollutants, including phenols, dyes and pesticides [18,4]. However, traditional Fenton processe requires chemical storage and transport of unstable H_2O_2 and the addition of Fe^{2+}. Beyond that, it was strictly limited by controlling pH, massive sludge production and high price of H_2O_2 [23]. Comparably, the developed electro-Fenton (EF), proposed to generate in situ H_2O_2 and Fe^{2+}, has drawn considerable attention as a promissory alternative technology by overcoming some drawbacks of traditional Fenton process [8]. However, external electricity input causes extra operating cost, which restricts its industrial applications. On the other hand, it has recently been shown that using these low soluble iron oxides as iron sources in the electro-Fenton process has the advantages of the ability to self-regulate the supply of a constant amount of iron ions and also the easy recycling of the iron catalyst after treatment [5]. Moreover, it can allow the electro-Fenton reaction to proceed under broader pH conditions [3,2]. Thus the process could be more useful and sustainable by developing Fenton-based systems that do not require either chemical addition or electrical grid energy.

Microbial fuel cell (MFC) is a newly developed bioelectrochemical system for simultaneous electricity generation and wastewater treatment. In MFCs, microorganisms oxidize the substrates to produce electrons in the anode chamber. The released electrons are conducted via an external resistor to the cathode, where they are consumed for the reduction of electron acceptor [17]. For an MFC using oxygen, the reduction of oxygen to H_2O requires a four-electron transfer, but it is also possible that oxygen reduction results in H_2O_2 production by a two-electron transfer reaction [7]. In the past decades, the power output of MFCs has increased to as high as several watt per square meter of surface area of electrode, making it practical to use MFCs as power sources for electro-Fenton systems with no external power supply [15,3,2]. It has been demonstrated that the bio-electro-Fenton (BEF) reaction in a MFC can efficiently dispose the bio-refractory and/or toxic compounds. Zhu and Ni [24] demonstrated the reaction of in situ

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generated H_2O_2 at a carbon felt cathode and Fe^{2+} released from adscititious scrap iron resulted in the formation of $^{\cdot}OH$ for degrading p-nitrophenol. Feng et al. [5] reported the complete decolorization and mineralization of Orange II by Fenton process in an MFC equipped with a carbon nanotube (CNT)/γ-FeOOH composite cathode. Rozendal et al. [13] have found that, in addition to power yield, it was also possible to synthesize H_2O_2 in the catholyte of a MFC system with noble-metal-free graphite as cathode material. Wang et al. [16] demonstrated the application of the MFC-Fenton technology to effectively remove estrone and sulfamethazine. However, up to date, no reports focused on treatment of actual industrial wastewater using bio-electro-Fenton system has been published.

Taking advantages of both the electro-Fenton reaction and utilization of bioelectrons as a power supply, in this study a MFC driven bio-electro-Fenton process was proposed for advanced treatment of coal gasification wastewater. To attain high degradation rates, $FeVO_4$/carbon felt (CF) was proposed to use as novel heterogeneous Fenton-like catalyst in the cathode of the MFC. $FeVO_4$/CF allows a facile recovery and recycling of the Fenton regent. More importantly, $FeVO_4$/CF containing iron ion and vanadate anion can be employed as a two-way Fenton-like catalyst. Such catalyst possesses a higher catalytic activity towards the degradation of refractory organic pollutants, compared with the conventional heterogeneous Fenton-like catalysts, such as α-Fe_2O_3, Fe_3O_4 and γ-FeOOH. The power generation, internal resistance and the concentration of the in situ generated reactive oxygen radicals in the MFC with $FeVO_4$/CF cathode were studied, then the BOD_5, COD, TOC and total phenols removal of the CGW was respectively examined. Moreover, the catalytic mechanisms of $FeVO_4$/CF in the BEF system were illustrated. This modified type of treatment system may provide a more energy-efficiency and cost-effective approach for industrial wastewater treatment.

2. Materials and methods

2.1. Preparation of $FeVO_4$/CF electrode

The preparation of the $FeVO_4$/CF composite cathode followed the method described elsewhere, with slight modifications [11]. Firstly, the carbon felt (CF, 4.0 cm × 4.0 cm, Liaoyang, China) used for the composite cathode was washed for 24 h in 5 M HCl to eliminate potentially catalytic foreign compounds from the CF's surface, and the washing process was repeated four times. After that, the ultrasonic treatment of the CF in the 4.27×10^{-2} M ammonium metavanadate, a 0.26 M solution of iron nitrate was quickly poured with a molar ration of 1:1. Finally, the composite electrode was rinsed with deionized water thoroughly and dried in nitrogen for use.

2.2. Operation and characterization of BEF process

A dual-chamber MFC, consisted of two chambers with an effective volume of 100 mL each, was separated by a proton exchange membrane (PEM, 4.0 cm × 4.0 cm, Nafion 212, Dupont Co., USA). The anode is a piece of carbon felt (4.0 cm × 4.0 cm × 0.5 cm) which was washed in a hot H_2O_2 (10%, 90 °C) solution for 3 h to develop local quinone sites on the carbon surface for improving the anode biocompatibility. The cathode was the composite electrode of $FeVO_4$/CF (4.0 cm × 4.0 cm × 0.5 cm). A Ti wire (0.5 mm in diameter) was used to connect the anode and cathode by passing through an external load, and all wire contacts were sealed with epoxy material. The distance between the electrode and the PEM was approximately 3.0 cm.

Inoculation was conducted with an adapted microbial consortium collected from the anode chamber of an existing MFC. The anode compartment of the MFC was flushed with N_2 for 10 min to ensure an anaerobic environment. The anodic solution contained (in 1 L deionized water): 4.0896 g Na_2HPO_4, 2.544 g NaH_2PO_4, 0.31 g NH_4Cl, 0.13 g KCl, and 12.5 mL trace metal solution and 12.5 mL vitamin solution. Glucose (700 mg/L COD) was fed as fuel substrate. The MFC reactor was started up according to the procedures as described in the previously reported studies [6].

For the control MFC, equipped with CF cathode (MFC-CF), O_2 was purged into the cathode chamber (electrolyte was 0.1 mol/L Na_2SO_4) at the rate of 100 mL/min to supply the oxygen needed for two-electron ORR. The solution pH was adjusted with dilute H_2SO_4 on 7.0. For treatment of CGW, the cathode solution consisted of $FeVO_4$/CF cathode (MFC-$FeVO_4$/CF), 100 ml CGW, and 0.1 mol/L Na_2SO_4. The other operational parameters were the same as the control MFC. Samples were taken from the cathodic chamber at different time intervals and analyzed for BOD_5, COD, TOC and total phenols. All of the experiments were conducted in triplicate with relative errors less than 10% at a controlled temperature of 30 °C and atmospheric pressure.

2.3. Power measurement and chemical analysis

Polarization and power curves were determined by varying the external resistance from 10 to 80,000 Ω. Values of the external resistance and corresponding voltage were measured by a digital multimeter (PMD-1608LS, MCC Corporation, USA). The current (i) was calculated, based on the voltage (V) and the external resistance (R), as $i = V/R$, and the power as $P = iV$. The internal resistance of the MFC was obtained as the gradient of the polarization curve over the range excluding concentration and activation polarization. The maximum power output was determined from the power curve [21]. Since the functional surface area of the electrodes could not be exactly determined, both current density and power density were normalized to the catholyte volume.

Cyclic voltammetry (CV) measurements at a scanning rate of 20 mV/s in the potential range of −1.2 V to +1.2 V were carried out using a CHI 660B electrochemical workstation (Shanghai Chenhua Instruments Corporation, China) equipped with a conventional three-electrode system [10]. If not stated otherwise, all potentials were reported against SCE (245 mV vs. NHE) in this study.

The concentrations of H_2O_2 in the cathode chamber were determined by spectrophotometric analysis using the iodide method at 352 nm. The concentration of reactive oxygen species generated in the cathode chamber was determined by using N,N-dimethyl-*p*-nitrosoaniline (RNO) [10]. BOD_5, COD, TOC and total phenols were measured according to Standard Methods [1]. The aforementioned measurements were conducted on an Agilent HP 8453 UV–Vis spectrophotometer.

3. Results and discussion

3.1. Performance of electricity production in BEF process

To study the performance of electricity production in BEF system with $FeVO_4$/CF as cathode (MFC-$FeVO_4$/CF), a control reactor with CF as the cathode (MFC-CF) was operated under the same conditions. Fig. 1 compared the cell voltage and power density curves of the two reactors. As shown, the maximum power density arrived 849.7 mW/m^3 in MFC-$FeVO_4$/CF system (185% higher than that of 298.1 mW/m^3 in MFC-CF system), which was corresponding to a current density of 2.6 A/m^3 at the voltage of 326.8 mV. Similarly, the open circuit voltage (OCV) obtained in MFC-$FeVO_4$/CF was 980.4 mV, 75% higher than MFC-CF (560.2 mV). Those results indicated that the MFC-$FeVO_4$/CF system can generate the similar level of electricity as the general reported two-chamber MFCs [14].

To further understand the cathodic reactions, electrochemical CV was performed at the $FeVO_4$/CF and CF electrode, respectively. As shown in Fig. 2, on the negative sweep at least two cathodic peaks were observed for the $FeVO_4$/CF electrode. The first peak at 0.88 V was confirmed to be the generation of H_2O_2 through a two-electron reduction of dissolved oxygen at the $FeVO_4$/CF cathode. This peak for the CF electrode was 0.78 V. The other two peaks at 0.32 V and 0.28 V were