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Chlorinated phenol treatment and *in situ* hydrogen peroxide production in a sulfate-reducing bacteria enriched bioelectrochemical system

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ABSTRACT

Wastewaters are increasingly being considered as renewable resources for the sustainable production of electricity, fuels, and chemicals. In recent years, bioelectrochemical treatment has come to light as a prospective technology for the production of energy from wastewaters. In this study, a bio-electrochemical system (BES) enriched with sulfate-reducing bacteria (SRB) in the anodic chamber was proposed and evaluated for the biodegradation of recalcitrant chlorinated phenol, electricity generation (in the microbial fuel cell (MFC)), and production of hydrogen peroxide (H_2O_2) (in the microbial electrolysis cell (MEC)), which is a very strong oxidizing agent and often used for the degradation of complex organics. Maximum power generation of 253.5 mW/m^2, corresponding to a current density of 712.0 mA/m^2, was achieved in the presence of a chlorinated phenol pollutant (4-chlorophenol (4-CP) at 100 mg/L (0.78 mM)) and lactate (COD of 500 mg/L). In the anodic chamber, biodegradation of 4-CP was not limited to dechlorination, and further degradation of one of its metabolic products (phenol) was observed. In MEC operation mode, external voltage (0.2, 0.4, or 0.6 V) was added via a power supply, with 0.4 V producing the highest concentration of H_2O_2 (13.3 g/L-m^2 or 974 μM) in the cathodic chamber after 6 h of operation. Consequently, SRB-based bioelectrochemical technology can be applied for chlorinated pollutant biodegradation in the anodic chamber and either net current or H_2O_2 production in the cathodic chamber by applying an optimum external voltage.

1. Introduction

Environmental contamination by toxic, recalcitrant, and xenobiotic compounds is a very serious global problem. Among these pollutants, chlorophenols (CPs) have garnered much attention because of their ubiquity in the environment and biota due to their extensive use in many industrial processes (Tobajas et al., 2012). CPs are the precursors or intermediates in many process industries, such as the dye, resin and plastics, pharmaceutical, and pulp and paper industries (Basak et al., 2013; Lim et al., 2013). They are widely used as paints, disinfectants, explosives, herbicides, pesticides, and fiber and leather preservatives (Gomez et al., 2009; Sahoo et al., 2010). CPs are irritants at low levels and have a very negative impact on the respiratory and central nervous systems at higher doses. They are regulated among the 65 priority pollutants by the United States Environmental Protection Agency (USEPA) because of their acute toxicity and carcinogenic properties (Zhao et al., 2015). Toxicity and bioaccumulation of CPs are largely linked to their lipophilicity. An increase in the chlorination of CPs increases their lipophilicity, which leads to greater potential for uptake into the organism. Moreover, the CPs with meta- and para-substituted chlorine generally are more toxic than ortho-substituted ones, as ortho-substituted chlorine shields the OH group that interacts with the active sites in aquatic organisms (Marković et al., 2015).

Because the removal of CPs from wastewater is a contemporary and very important issue, physical, chemical, and biological methods, including adsorption on activated carbon or sludge, chemical or enzymatic oxidation, catalytic degradation, solvent extraction, and microbial degradation, have been proposed for removing or degrading several CPs from wastewaters (Monsalvo et al., 2012; Munoz et al., 2016; Wang et al., 2016). Despite this extensive research, suitable, vigorous, and low-cost treatment of these pollutants has yet to be implemented. Therefore, efficient

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treatment methods of industrial wastewaters should be developed to prevent the discharge of CPs into downstream waterbodies, so that this environmental concern can be effectively addressed.

In the last decade or so, bioelectrochemical systems (BESs), such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), have been widely investigated for their novel aspects and potential environmental advantages (Rozendal et al., 2008; Zhang and Angelidaki, 2014). The basic principal of such systems is the oxidation of organics from wastewater by electrochemically active microorganisms, and, consequently, the microorganisms transport electrons resulting from this oxidation to the anode via extracellular electron transfer. Then, the electrons are transported to the cathode through an external circuit, where they are used for oxygen reduction and electricity generation (in MFCs) or other useful product formation, such as hydrogen (H_2), caustics (NaOH/KOH), and hydrogen peroxide (H_2O_2) (with additional power supply in MECs). Overpotential can be substantially brought down with electrochemically active bacteria (EAB) at the anode/cathode, hence inexpensive materials (such as graphite and carbon) can be employed as electrodes in BESs (Mu et al., 2009). A number of valuable oxidation or reduction reactions demonstrating the versatility of BESs have been described. Bioelectricity generation can be achieved by using a large range of biodegradable fuels, including substrates such as acetate (Min et al., 2005) and organics in wastewater (Min and Logan, 2004; Shimoyama et al., 2008). Meanwhile, some studies have reported that BESs could greatly promote the removal of refractory organics such as pyridine, quinoline, indole, furfural, and phenol (Hu et al., 2011; Luo et al., 2010; Song et al., 2014). At the BES's anode, co-substrates (e.g. glucose for phenol and pyridine (Luo et al., 2009; Zhang et al., 2009), acetate and phenol for pentachlorophenol (Huang et al., 2011), brewery waste for azo dye (Miran et al., 2015)) provide electrons for the degradation of biorefractory compounds at higher rates, along with electricity production (in MFC) or useful product formation (in MEC); therefore, both electricity production/useful product formation and the degradation of biorefractory compounds are major focuses of BESs.

Earlier studies have mainly investigated the reduction of CPs, such as 4-CP, at the abiotic cathode of an MFC; during this process, electricity was simultaneously generated (Gu et al., 2007; Wen et al., 2013). The limitation in these studies was that only dechlorination took place and no further mineralization occurred. Only a few researchers have given attention to aromatic chlorides in MFCs with microbial anodes. The microbial cultures in such anodes play a significant role in the overall performance of the BESs. Sulfate-reducing bacteria (SRB) have been exploited successfully for the biodegradation of phenolic and other persistent organic pollutants in anaerobic processes (Haggblom and Young, 1995; Meckenstock et al., 2000). Lately, some researchers have used SRB for current generation with simultaneous organics oxidation and sulfate reduction, because of their electroactive nature in BESs (Cordas et al., 2008; Kang et al., 2014). Using an enriched SRB culture in a BES's anodic chamber for the treatment of toxic pollutants, such as 4-CP, may be an attractive option that will help in the efficient degradation of the pollutant, along with bioelectricity generation or other useful products formation.

On the other hand, as stated earlier, a number of useful products can be produced at the cathode in MECs. Among these products, H_2O_2 is seen as a viable option based on life cycle assessment (LCA) testing, with significant environmental benefits through the displacement of chemicals produced by conventional means (Foley et al., 2010). H_2O_2 is environmentally friendly, as its degradation products are only water and oxygen, with no hazardous residues (Li et al., 2016). H_2O_2 has been applied (as a part of Fenton's reagent) to numerous industrial areas (including where CPs are involved) such as chemical synthesis, pulp paper and textile bleaching, medical disinfection, treatment of wastewater, and destruction of hazardous organic wastes (Khataee et al., 2011; Siedlecka and Stepnowski, 2006). Therefore, CPs removal and *in situ* H_2O_2 production could be a viable option in BESs. Recently, a few researchers tried to produce H_2O_2 *in situ* in BESs (a bioelectro-Fenton system) or *ex situ* along with treatment of pollutants (such as dye) (Ling et al., 2016; Liu et al., 2012). The *in situ* production of H_2O_2 in comparison to the commonly used anthraquinone oxidation method (which requires the use of hydrogen and non-aqueous solvents with significant energy input and generates substantial waste along with possible hazards due to transportation (Campos-Martin et al., 2006)) will likely be more secure and efficient, as there are no transports or handling issues.

Therefore, the overall objectives of this study were to enrich the SRB-dominated microbial community and to assess its capacity to biotransform 4-CP and produce current/H_2O_2 in batch-fed BESs. The effect of the initial 4-CP concentration on the performance of the BESs in terms of bioelectricity generation and organics and sulfate removal were evaluated, and optimum externally added voltage conditions were determined for maximizing H_2O_2 production.

2. Materials and methods

2.1. MFC and MEC reactor setups

The MFC was developed with two equally sized rectangular Plexiglass chambers. Each chamber had a volume of 200 mL. The anode was carbon felt (3.18 mm thick, 5 cm × 5 cm; Alfa Aesar, Haverhill, USA). The cathode was carbon cloth, purchased from Fuel Cell Earth (Wakefield, USA), with a surface area of 25 cm^2, containing 1.0 mg/cm^2 (20 wt.%) Pt on conductive specialty carbon black (XC-72), and Nafion treated to avoid any damage of the Pt catalyst from the catholyte. The anode and cathode were separated by a cation exchange membrane (Nafion 117, Dupont Co., USA), which was treated with H_2O_2, H_2SO_4, and deionized water under boiling condition prior to application between electrodes to enhance performance (Miran et al., 2016a). The system was sealed to ensure an anaerobic environment in the anode. A pure nitrogen gas bag was attached to the anodic chamber to prevent ingress of atmospheric oxygen into the chamber. For the MEC only, the cathode was replaced with graphite felt having the same dimensions as that of the carbon felt. During MEC operation, external voltage was provided by a power supply (Model 2231A-30-3, Keithley Instruments Inc., USA).

2.2. Inoculum, anolyte, and catholyte

An SRB culture was enriched with anaerobic sludge collected from a domestic wastewater treatment plant (Sincheon wastewater treatment plant) in Daegu, South Korea. The sludge was inoculated into modified Postgate's B medium (contained the following (in mM): KH_2PO_4 3.7, NH_4Cl 18.7, $FeSO_4{\cdot}7H_2O$ 0.4, $MgSO_4{\cdot}7H_2O$ 0.2, yeast extract 3.6, sodium citrate 1.2, ascorbic acid 0.6, and thioglycollic acid 1.7 with sodium lactate and sodium sulfate) as the main carbon and sulfate sources, respectively (lactate COD/SO_4^{2-} mass ratio of 2.0). Lactate COD/SO_4^{2-} mass ratio was kept constant in all experiments for comparisons. Sodium 2-bromoethanesulfonate (Na-BES) (2.5 g/L (11.8 mM)) was added at the enrichment stage to suppress acetoclastic methanogenic activity, which can consume lactate in the medium and adversely affect a BES's performance. A trace element solution (1.0 mL) was also added. Prior to culture enrichment, the medium was autoclaved at 15 psi and 120 °C for 20 min and deoxygenated by bubbling with high purity nitrogen to