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Electricity generation and recovery of iron hydroxides using a single chamber fuel cell with iron anode and air-cathode for electrocoagulation

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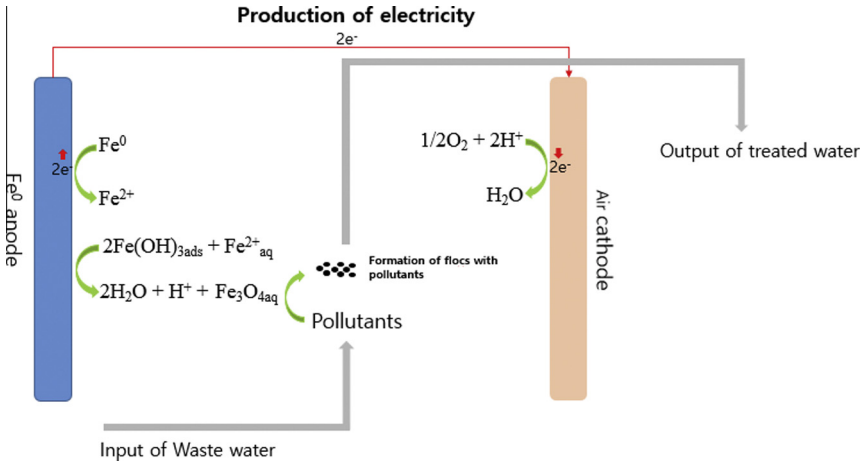
HIGHLIGHTS

- This iron–air fuel cell can replace traditional electrocoagulation water treatment.
- Main reactions were investigated to produce electricity and iron hydroxides.
- An initial pH 5 was the optimal condition for producing maximum power density.
- The power density output can reach up to 4343 mW/m^2.
- Iron hydroxides with magnetite and maghemite were recovered at initial pH 7.5–8.5.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of a single chamber fuel cell with an iron anode and air cathode is a new and innovative concept in electrocoagulation. In this study, we investigated the predominant reactions that contribute to the production of electricity and iron hydroxides in solution. Solutions composed of 0.06 M $NaHCO_3$ and 0.05 M NaCl at an initial pH of 5 were determined to be optimal for producing the maximum power density of 1997 mW/m^2 after 24 h. Increases in the bicarbonate concentration and ionic strength of the solution induced a corresponding decrease in the anode potential and increase in the cathode potential, which resulted in an increase in the cell potential and power density. Further, increasing the $NaHCO_3$ concentration to 0.1 M and the ionic strength of the solution to 0.56 M induced an increase in the maximum power densities to 2436 and 4343 mW/m^2, respectively. Initial pH values of 7.5 and 8.5 in solutions containing 0.06 M $NaHCO_3$ and 0.05 M NaCl were employed to synthesize magnetic iron hydroxides including magnetite and maghemite. These results suggest that this fuel cell technology can be used not only for electrocoagulation with the removal of contaminants, but also for producing useful products such as electricity and magnetic iron hydroxides. Advances in waste water air-metal fuel cells will enable more efficient power generation and systems suitable for scale-up.

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1. Introduction

Microbial fuel cells (MFCs) are an emerging technology used to produce electricity as well as treat waste water. Aided by microbes, MFCs are capable of converting the chemical energy stored in nearly all chemical compounds to electrical energy [1–5]. Over the last decade, various configurations of MFCs have been developed including single chamber MFCs, dual chamber MFCs with membranes, tubular MFCs, plate MFCs, and stacked MFCs [6–10]. Furthermore, a nano composite electrode has been recently developed in efforts to enhance power density [11,12]. As a result, the power density of MFCs has increased by 10,000 orders of magnitude [12–14]. However, owing to the metabolic requirements of bacteria, MFCs can only be operated at neutral pH, and the generated power density is usually lower than about 2000–3000 mW/m^2 [3,15]. Therefore, in order to overcome the shortcomings of MFCs, Cr–methanol fuel cells have been developed to remove Cr (VI) with higher power density output [15]. In this context, we conducted a study on a novel iron–air fuel cell for electrocoagulation.

Electrocoagulation is an electrochemical technology for the treatment of waste water. Iron and aluminum have been widely used as electrode materials in electrocoagulation systems, because these materials are cheap and have been demonstrated to be very effective for the electrocoagulation process [16]. Iron or aluminum oxides as flocculating agents are generated by the electrooxidation of a sacrificial iron or aluminum anode. Therefore, electrocoagulation is effective for the removal of metals such as Pb, Cd, Cr, As, Mn, Cu, Zn, Ni, Al, Fe, Co, Mg, Ca, and Pt. Electrocoagulation has also been employed for removing anions such as CN^-, PO_4^{3-}, SO_4^{2-}, NO^{3-}, F^-, and Cl^-, organic compounds such as total petroleum hydrocarbons (TPHs), toluene, benzene, xylenes (TBX), methyl tert-butyl ether (MTBE), chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids, clay minerals, organic dyes, oil, and greases from a variety of industrial effluents [17–22]. Meanwhile, the use of iron anode in membrane bioreactors (MBRs) with electrolytic cells [23,24] and MFCs [25] indirectly assisted waste water treatment, such as the removal of COD and triclosan, by improving membrane fouling reduction.

Furthermore, electrocoagulation is one of the most effective methods for the treatment of acid mine drainage (AMD) containing heavy metals [26]. AMD is a persistent environmental problem in many active as well as abandoned sulfide and coal mine sites. AMD is generated by pyrite and other sulfide minerals upon exposure to oxygen and water, and in the presence of oxidizing bacteria, which oxidize the mineral to produce dissolved metals, sulfate, and acidity [27]. Low pH and elevated concentrations of metal ions (e.g. Fe^{2+}, Mn^{2+}, Al^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, etc.) and oxyanions (CrO_4^{2-}, AsO_3^-, etc.) often characterize these discharges [28]. Discharged mine waters can be treated actively or passively by a combination of both methods [29]. An alternative approach for treating AMD is based on the use of a new type of fuel cell that was recently proposed [30]. Two chamber cells with carbon cloth anode and air-carbon cloth cathode separated by an anion exchange membrane was used. In these cells, the ferrous ions are oxidized to iron hydroxide at the anode surface, while oxygen is reduced at the cathode. Based on this study by Logan's research group [30], a few other studies on air cathode fuel cells for treating ferrous iron have recently been conducted [31–34].

In the current work, we used a single chamber air-cathode fuel cell with a sacrificial iron plate anode, which combined the concepts of electrocoagulation and fuel cells to treat waste water and produce electricity. In addition, we used the concept of "fuel cells" instead of "batteries", although it was possible to produce electricity without external fuel input. The main objective of this system is to treat waste water containing contaminants (Fe^{2+}, AsO_3^-, NO_3^-, etc.) that can oxidize or reduce on the surface of the electrodes and thereby affect the electrode potential. The iron plate is oxidized at the anode and oxygen is reduced at the cathode, as shown in reactions (1)–(3).

		E^0	
Cathode:	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	1.23 V	(1)
Anode:	$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	0.44 V	(2)
Net reaction:	$1/2O_2 + 2H^+ + Fe_{(s)} \rightarrow H_2O + Fe^{2+}$	1.67 V	(3)

The generation of iron hydroxide on the iron surface by the oxidation of ferrous ions, caused passivation on the surface of the iron anode [35–42]. In addition, the dissolved iron generated by the oxidation of the iron anode may be transported towards the air cathode. Therefore, the main reactions that occur in a single chamber cell with the air-carbon cloth cathode and iron plate anode are more complicated, and have been investigated in this study.

Furthermore, since magnetic oxides such as magnetite can be separated from water in the presence of a magnetic field, it is useful to treat waste water with heavy metals through complexation of these on the surface of magnetite and subsequent magnetic separation [42]. However, Cheng et al. [31] attempted to recovery iron oxides from synthetic AMD using fuel cells, and demonstrated the feasibility of synthesizing goethite, but not magnetite. Therefore, in the current work, we attempted to recover magnetic iron hydroxides using a new fuel cell system with an iron plate anode.

In this study, we employed a single chamber fuel cell with an iron anode and air cathode as a replacement for traditional electrocoagulation for water treatment. Since this concept of iron–air fuel cells for electrocoagulation is unprecedented, an understanding of the basic principles of production of electricity and recovery of iron hydroxides is necessary. Therefore, the system described herein (Graphical abstract and Fig. S1 in the Supporting Information (SI)) is a very basic type of fuel cell that has been used to examine factors that can affect the production of electricity and iron hydroxides in solution. For achieving these primary objectives, electricity generation, polarization curves, and power density have been investigated by measuring the electrode potentials at varying external resistances, initial pH, bicarbonate concentration, and ionic strengths of the solution. The composition of Fe generated on the surface of the electrodes and in the solution was also investigated by Raman spectroscopy. Based on the results of the study, the main principles of power production and the feasibility of recovery of magnetic iron oxides were investigated. In addition, arsenate was selected as a representative contaminant and treated to investigate the applicability of the current fuel cell system in heavy metal contaminant removal.

2. Experimental

2.1. Construction of a single chamber fuel cell with iron anode and air cathode

The reactor used for the experiments consisted of a chamber with an anode and cathode. The surface area of the electrode plates, chamber volume, and distance between the electrodes were 25 cm^2, 90 mL, and 3 cm, respectively (Fig. S1). The anode was placed on one end of the chamber and covered with a plastic end plate, whereas the cathode was placed at the other end and covered with another end plate with a center hole (4 cm × 4 cm). Titanium wires (1 mm in diameter) were used to connect the two electrodes. In addition, Ag/AgCl reference electrode was used to measure the cathode and anode potentials. At 25 °C, the potential