Effects of supporting electrolytes in treatment of arsenate-containing wastewater with power generation by aluminumair fuel cell electrocoagulation

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A B S T R A C T

Aluminum–air fuel cell electrocoagulation was evaluated for arsenate removal during power production. Effects of operational parameters (type and concentration of individual and mixed supporting electrolytes and initial pH) were investigated. $1 \, mg \, L^{-1}$ arsenate in 1 L of anolyte (with 10 mM NaCl) was reduced to $1 \, \mu g \, L^{-1}$ in 4 h, power density produced was $112 \, mW/m^2$. 8 mM Na_2SO_4 mixed with 10 mM NaCl created optimal conditions as mixed supporting electrolyte. Power density increased to $308 \, mW/m^2$ and arsenate was reduced to $15 \, \mu g \, L^{-1}$ after 24 h. This indicates aluminum–air fuel cell electrocoagulation is useful treatment process.

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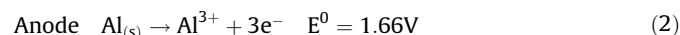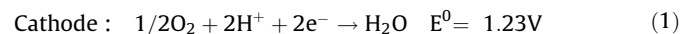
Introduction

Arsenic contamination in natural water bodies (ground and surface water) is a worldwide problem and poses a great threat to the human being and aquatic life [1,2]. The mine drainage and geothermal discharge, arsenical pesticides uses, arsenic containing fly ash disposal, and mineral dissolution are the main sources for the release of high concentration of arsenic in the natural water [3,4]. Naturally, arsenic can be found in more than 300 different mineral forms, among them the predominant arsenic species in groundwater are Arsenate (As(V)) and arsenite (As(III)). Arsenate is known as a soft acid encompassing $AsO4^{3-}$, $HAsO_4^{2-}$, and H_2AsO^{4-} species and the distribution between these species is determined by redox potential and pH [5,6]. Therefore it is important that arsenate containing wastewater should be treated before discharge.

The different types of treatment technologies have been used for arsenate containing wastewater treatment, comprising electrocoagulation [7,8], coagulation and precipitation with iron and aluminum sulphate [2], adsorption [1,9,10], photocatalysis [5,11], ion exchange [12,13], ultrafiltration [14], and bioleaching [15,16]. These all technologies are effective for arsenic containing wastewater treatment but there are some limitation with respect of energy input and these are not cost effective.

Electrocoagulation is a simple and efficient electrochemical process that uses flocculating agents produced by oxidation of sacrificial aluminum or iron electrodes. Electrocoagulation has been successfully used to treat different kinds of wastewater, such as acid mine drainage discharge and industrial effluent, as well natural water. The electrocoagulation process is applied to remove a wide range of pollutants, such as arsenic, chromium, phosphate, nutrients, color, fluoride, and chemical oxygen demand [17–22]. Sacrificial aluminum and iron electrodes have been widely used in electrocoagulation because they are inexpensive and can be efficiently oxidized to produce flocculating agents. Most researchers have preferred to use sacrificial aluminum material as electrodes in the electrocoagulation process for arsenic-containing wastewater treatment [23–26]. Iron is more corrodible than aluminum, and it has been suggested that complex precipitants of iron–arsenic can cause oxidative hepatic damage in humans [27]. In this context, we conducted this study on the treatment of arsenic-containing wastewater using a single-chambered aluminum anode and air-cathode fuel cell.

$$\text{Cathode}: \quad 1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^0 = 1.23V \tag{1}$$

$$\text{Anode} \quad Al_{(s)} \rightarrow Al^{3+} + 3e^- \quad E^0 = 1.66V \tag{2}$$

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Net reaction : $1/2O_2 + 2H^+ + Al_{(s)} \rightarrow H_2O + Al^{3+}$ $E^0 = 2.89V$

$$(3)$$
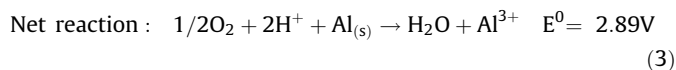
Because the high energy demand of the applications of electrocoagulation have been limitation of their use, energy costs need to be reduced to make this process more practicable [19]. Therefore, an alternative approach has been proposed based on the combined concept of electrocoagulation and a fuel cell to treat wastewater and produce electrical power [28]. A single-chambered air-cathode fuel cell consists of a sacrificial iron plate anode and an air-carbon cloth cathode, wherein oxidation of the iron plate and reduction of oxygen occur at the anode and cathode electrode surfaces, respectively [28]. A few other studies on air-cathode fuel cells have recently been conducted [19,29–33]. Furthermore, the addition of supporting electrolytes is necessary for the use of air-cathode fuel cells to increase the ionic conductivity of the solution as well as to improve the corrosion rate of the anode electrodes. Different types of supporting electrolytes, such as NaCl, NaHCO$_3$, and Na$_2$SO$_4$, have been used to determine the most favorable supporting electrolytes for the electrochemical process.

According to the results of previous studies, the addition of a supporting electrolyte is a major factor in the electrochemical process because the supporting electrolyte increases the ionic conductivity of the solution, which leads to improvement of the removal efficiency of the electrochemical process due to an increase in the corrosion rate of the aluminum electrode [34,35]. Most researchers have stated that NaCl could be the best supporting electrolyte because Cl$^-$ has a tendency to break down the passive film formed on the aluminum anode electrode surface and remarkably increases the current density during the electrocoagulation process [35–37].

It was recently observed that a high concentration of supporting electrolyte was required to improve the cell voltage and the removal efficiency of the fuel cell with the use of an air-cathode fuel cell [28–32,38]. The need for this high concentration of supporting electrolyte is one of the challenges for practical application of this kind of fuel cell. Based on previous research, we used a single-chambered aluminum–air fuel cell electrocoagulation in this study. We investigated the effects of several parameters including type and concentration of supporting electrolyte, such as NaCl, Na$_2$SO$_4$, and NaHCO$_3$, and initial pH of the electrolyte for the performance aluminum–air fuel cell electrocoagulation. The concentration of arsenate was 1 mg L^{-1}, and the volume of the total solution was 1 L.

Experimental methods

Materials

Sodium arsenate heptahydrate (NaH$_2$AsO$_4$·7H$_2$O), sodium chloride (NaCl), sodium bicarbonate (NaHCO$_3$), and sodium sulfate (Na$_2$SO$_4$) were used to produce wastewater. The aluminum plate was 0.25 mm thick and 99.5% pure with a surface area of 25 cm^2. The cathode was a commercial air cathode (MEET Ltd.) consisting of three layers. The catalytic layer (CL) was produced from a mixture of active carbon powder, manganese oxide catalyst powder, and polytetrafluoroethylene binder. The current collection layer (CCL) was a woven nickel mesh. The gas diffusion layer (GDL) was a porous Teflon film. All of the air cathodes tested in this study were cut from a large air cathode sheet.

Ag/AgCl reference electrodes (model MF-2052, Bioanalytical Systems, Inc., USA) were used to quantify the electrode potential.

Reactor

The single-chambered fuel cell consisted of 90 mL of working volume and was constructed based on our previous design [28]. A zero-valent aluminum plate and an air-carbon cloth were used as the anode and cathode electrodes, respectively. The working chamber was connected to an external reservoir containing 1 L of electrolyte with continuous recirculation at a flow rate of 40 mL min^{-1} (as shown in graphical abstract). The reactor was first operated in open-circuit mode for 5 min to measure the open circuit voltages of the anode and cathode, and then the fuel cells were connected at an external resistance of 20 Ω.

Experimental procedures

The chemicals used were of analytical grade. The relevant anolyte solution was prepared by dissolving NaH$_2$AsO$_4$·7H$_2$O and NaCl, Na$_2$SO$_4$, and NaHCO$_3$ in deionized water. HCl and NaOH were used to adjust the pH of the solution to the required initial pH. A data logger (model VR-71, T&D Co., USA) was used to record the total cell voltage at 10 min intervals with fixed 20 Ω external circuit resistance and 30 °C temperature for all experiments. The first experiment was conducted to investigate the effects of three individual electrolytes: NaCl, Na$_2$SO$_4$, and NaHCO$_3$. The second experiment was performed to examine the combined effects of supporting electrolytes, such as NaHCO$_3$:NaCl and Na$_2$SO$_4$:NaCl. The third experiment was conducted to investigate the effects of initial pH (5, 7, and 9) on fuel cell performance. The volume of 1 L of wastewater with continuous recirculation, an initial pH of 7, 1 mg L^{-1} arsenate, and an external resistance of 20 Ω were kept constant in all experiments.

Analysis

Through experiments, the performance of an aluminum–air fuel cell electrocoagulation was characterized by electricity generation, polarization curve, and power density. The current density, power density, and total current produced during the 24-h experiment at 20 Ω external resistance were calculated based on the following equations:

$$i = V/(R_{ex}A), \qquad (4)$$

$$P(mW/m^2) = 10iV, \qquad (5)$$

$$I = V/R_{ex}, \qquad (6)$$

where A (cm^2) is the surface area of the anode electrode, V (mV) is the voltage, and R_{ex} (Ω) is the external resistance (a factor of 10 is needed for the given units).

The total dissolved aluminum ions produced into the solution after 24 h of treatment time was estimated in three different form such as Al$_{cal}$, Al$_{mea}$, and ΔAl. Where Al$_{cal}$ (mg L^{-1}) is the total calculated aluminum ions, Al$_{mea}$ (mg L^{-1}) is the total measured aluminum ions, and ΔAl (mg L^{-1}) is the difference of calculated and measured aluminum ions and occurrence of ΔAl into the solutions indicated the availability of dissolved aluminum in the form of stable aluminum hydroxides. In this research Al$_{cal}$ after 24 h of treatment time was estimated using Faraday's law as follows:

$$m = \frac{I \times t \times M}{Z \times F}, \qquad (7)$$