Treatment of surface water contaminated arsenite using continuous flow air-cathode electrocoagulation

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Abstract. Air-cathode Electrocoagulation (ACEC) is a new emerging technology that combines the concepts of electrocoagulation and fuel cell technology for treating water contaminated by pollutants without the addition of external energy. In this study, the ACEC reactor was used for the removal of Arsenite (As³⁺) contained in river water. The effects of the different anode materials and hydraulic retention time (HRT) to the performance of the reactor were investigated. The water containing 3,5 ppm of arsenite was used as a representation of river water contaminated by heavy metal. Three types of metal plates (magnesium, iron, and aluminum) were used as anode materials, while a wet-proof (30%) carbon cloth used as a cathode electrode. The reactor performance was evaluated by measuring the removal efficiency of arsenite, metal hydroxide concentration, current density, and maximum power density of the reactor. The result showed that the ACEC reactor with iron, aluminium, and magnesium anode were able to remove 99%, 17%, and 73% of arsenite respectively. In further experiments, the reactor was conducted in continuous mode with 4, 8, and 12 hours of HRT. The ACEC reactor with 12 hours HRT was able to remove arsenite up to 99% for 24 hours. This result indicated that ACEC process is a promising technology for the effective removal of arsenite from aqueous solution without additional energy.

1 Introduction

The occurrence of arsenic in drinking water sources currently use surface water sources is a worldwide problem. Arsenic is a carcinogenic metal that is found in surface water and naturally found in surface water, especially in waters exposed to a volcanic eruption. However, the concentration of arsenic in waters has increased with the development of the industry [1].

Arsenic can provide harm to the body because it is carcinogenic. The arsenic metal can cause diseases such as respiratory system disorders, gastrointestinal disorders, skin cancer, disorders of the nerves, to obstructive pulmonary disease.

Several previous studies have found to treat heavy metal such as ion-exchange, adsorption, chemical precipitation, and electrocoagulation. Electrocoagulation technology is a technology that is widely used because it has high allowance effectiveness [2]. However, electrocoagulation is more suitable for use in urban areas than in rural areas because it needs some external electricity supply. For this reason, modifications are made through new technology, namely Air-Cathode Cell Electrocoagulation (ACEC) which in its application does not require external energy so it is expected to be more economical compared to the conventional electrocoagulation technology [3]. The reaction is shown in the following reactions.

Recently, ACEC treatment for arsenic removal has been investigated by some research groups [4, 5, 6]. These groups used ACEC to remove 1 liter of 1 mg/L As(V) with

an air cathode and a carbon cloth. In this research, we investigated the effectiveness of ACEC technology in the removal of arsenite (As(III)) without supporting electrolyte addition. Most of As(III) removal needs to convert As(III) to As(V) to get higher efficiency [7].

The performance of ACEC reactor with different anode materials, initial pH, and HRT to investigate the most effectiveness conditions in the mechanism of arsenite removal in water. In addition, the electrical potential that can be generated from the arsenite removal process using ACEC technology was analyzed. Most importantly, we provided a performance evaluation of diverse methods with respect to arsenite removal efficiency, current electricity produced, and the maximum power density of the reactor.

2 Methods

2.1 Reactor construction

The reactor used was made of acrylic material with a total volume of 75 ml (**Figure 1**). Three types of metal plates were used as an anode electrode (aluminum, iron, and magnesium). Each plate has a thickness of 2 mm with an area of 25 cm². A wet-proof (30%) carbon cloth used as a cathode electrode. The source of arsenic metal was As³⁺ species from the solution of NaAsO₂. The concentration of arsenic was 3.5 ppm refers to the maximum arsenic concentration found in surface water in the Ciwidey Area, Bandung, Indonesia.

2.2 Reactor operation

In the first experiment, the reactor was operated in the fed batch-recirculation mode using a peristaltic pump with a

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flow rate of 75 ml/min with an external resistance of 20 Ω . The volume of treated water was 2.0 liters. The sample was taken for 0.5, 1.0, 2.0, 3.0, 4.0, 8.0, 18, and 24 hours. The species of the arsenic i.e. arsenite and arsenate were also analyzed. In the further experiment the reactor was operated in the continuous flow mode with 4, 8, 12 hours of HRT. The reactor was operated using magnesium metal plate as the best anode material.

Fig. 1. Air-cathode electrocoagulation reactor.

2.3 Analysis and Calculation

Parameters analyzed were arsenic concentration and anode metal plates dissolved in the system. The treated water sample is filtered to separate the dissolved metal from the formed precipitate. Then the samples were analyzed using AAS (Atomic Absorption Spectroscopy).

As(III) analysis was performed using colorimetric method on the basis of spectrometry. Total arsenic concentrations of (As(III) + As(V)) were determined using an (AAS) atomic adsorption spectrometer (SCIEX Perkin Elmer Elan mode 5000).

For the analysis of precipitate formed using FTIR (Fourier Transform Infrared Spectroscopy) and SEM-EDS (Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy). Precipitate analysis was carried out to prove that the arsenite removal process has changed from a solution to a solid.

To measure the electrical potential in the ACEC reactor, the cathode and anode were connected to a voltmeter using a 1 mm diameter titanium wire. To analyze the electricity production from the reactor, the current and voltage data were collected. Those data used for polarization curve analysis to see the maximum electricity generated on the reactor. The polarization curve was made of two variables, current density and power density which the calculations use the following equation.

$$I = \frac{V}{R_{ex}} \quad (3)$$

$$i = \frac{I}{A} \quad (4)$$

$$P = V \times I \quad (5)$$

$$p = \frac{P}{A} \quad (6)$$

Where I is current, R_{ex} is external resistance, i is current density, A is area, P is power, p is power density. The polarization curve is made by varying external resistance (20-15,000 Ω). From the analysis of the polarization curve obtained the maximum value of power density.

3 Results and discussion

3.1 Characterization of ACEC-produced precipitate

At first, arsenite solution was clear and colorless. During the process, flocs will be produced and turned the solution into a turbid and reddish-brown solution. Based on research from [4], the removal of As (III) through the oxidation process of As (III) to As (V), followed by co-precipitation of As (V) with the anode metal hydroxides [4].

Based on **Figure 2(a)**, It shows the broad O-H stretching band in the 3000 to 3700 cm^{-1} range. The peak at 3695.61 and 3448.72 cm^{-1} reflects hydroxyl groups and their corresponding -OH stretching for magnesium hydroxide and oxyhydroxides phases. The absorptions within 1340-1470 cm^{-1} correspond to C-H stretching vibrations. The peak at 864.11 cm^{-1} was assigned to the symmetric stretching vibrations of As(V)-O structural units [8].

Figure 2(b) shows the iron-arsenic by-product. The bands at 3404.36 and 2964.59 cm^{-1} are generally assigned to OH stretching. Bands for hydroxyl bending and $\gamma(\text{OH})$ water bending vibration showed up at 1631.78 cm^{-1} [8]. Lepidocrocite phase, magnetite (Fe_3O_4), and Fe-O at 1101.35, 1631.78, and 468.70 cm^{-1} , respectively. Lepidocrocite was the main product of iron and NaCl reaction [8]. The 804.32 cm^{-1} band was assigned by Loehr and Plane [9] to the stretching vibration of the As-O bond.

Based on **Figure 2(c)**, it shows that there is a wide O-H stretch in the range of 3000 to 3700 cm^{-1} . The peak at 3412 cm^{-1} reflects the hydroxyl group and the -OH stretch which is thought to be aluminum hydroxide and shows the boehmite characteristics. While the peaks at 1440 and 1631 cm^{-1} correspond to the vibrations of the boehmite amorphous group. Meanwhile, the peak at 812.03 cm^{-1} is indicated as an As (V) -O structural unit [8].

The SEM (Scanning Electron Microscope) technique has most widely been used to identify the morphology of electrocoagulation precipitate. In this research, the SEM was used to investigate the morphology of the ACEC precipitate produced during the process. Based on the SEM analysis in the **Figure 3**, the precipitate produced has superb porosity with the size was ~100 nm. It can be classified into nanopores and micropores. Due to the larger surface, the metal oxide/oxyhydroxides can adsorb the arsenite aqueous easily [5].

Fig. 2. Basic characterization of ACEC precipitate using FTIR (a)magnesium-arsenic precipitate analysis (b)iron-arsenic precipitate analysis (c)aluminum-arsenic precipitate analysis.

Fig. 3. SEM analysis of ACEC produced precipitate.

The EDX analysis in **Figure 4** showed the ACEC precipitate confirmed the presence of Fe, As, and oxygen (O) as a major element. The weight percentages of Fe, As, and O were 62.05, 6.63, and 31.32%, respectively. The appearance of arsenic peaks in the EDX spectrum after the As treatment suggests that the As should be adsorbed on the surface of the iron-oxyhydroxides

Fig. 4. EDX analysis of ACEC produced precipitate.

3.2 Power and current density production in ACEC reactor with different anode

The effects of anode was investigated by varying the magnesium, iron, and aluminum plate. To distinguish with the previous research, the arsenite treatment was investigated without supporting electrolyte. This type of research was conducted to explore the practicality of ACEC system to treat drinking water in remote areas. Because it is found that the need for electrolyte is one of the major challenges to expand the use of ACEC systems. Therefore, in this work, we explore the possibility to optimize the system with low conductivity, referring to the characteristics of the real river.

Based on the **Figure 5**, the highest current produced was about 1.8 mA by magnesium plate. Aluminum and iron were lower of about 0.15 and 0.25 mA.

Fig. 5. The current produced with time (2 Liter of NaAsO₂, pH 7).

Figure 6 showed that the highest power density production reached by magnesium plate 0.103 W/m². Comparing to aluminum and iron plate which have value 0.004 and 0.011 W/m². Magnesium has the smallest redox potential value (-2.37 E⁰), compared to aluminum (-1.66

E^0) and iron ($-0.44 E^0$). The tendency for metals to oxidize increases if the redox potential value becomes smaller. This makes magnesium most reactive so that the highest electrons are produced.

Fig. 6. Power density versus current density for magnesium, aluminum, and iron anode (Insert : aluminum anode).

3.3 Performance of ACEC reactor with different anode materials

In this experiment, the conductivity of the solution was adjusted around $30\text{--}50 \mu\text{S/cm}$. The initial pH was neutral (7) and the initial arsenic concentration was 3.5 ppm.

In the removal of As(III) process, the concentration of As(V) and total arsenic was also detected. It is seen from Figure. 7 that the As(V) was produced and the concentration of As(V) increased with the reaction time and subsequently decreased with the time.

In Figure 7, iron anode has the best performance among others anode plate. Iron can remove arsenic until $<0.05 \text{ ppm}$ in 24 hours. Comparing with aluminum and magnesium plate which still leaves arsenic concentration around 2.8 ppm and 0.9 ppm, respectively. Based on equation 7-9, the removal of arsenic is directly linked to the rate of coagulant formation with the oxidation of the metal anode electrode. It can be explained with the solubility coefficient number of the three anodes (Table 1). $\text{Fe}(\text{OH})_{3(s)}$ has the smallest solubility constant among others so it will be produced first and can remove arsenite faster than others.

Table 1. Solubility constant of metal hydroxides.

Compound	Solubility Constant K_{sp}	Reference
$\text{Fe}(\text{OH})_{3(s)}$	4×10^{-38}	[10]
$\text{Al}(\text{OH})_{3(s)}$	1.3×10^{-33}	
$\text{Mg}(\text{OH})_{2(s)}$	1.8×10^{-11}	

(a)

(b)

(c)

Fig. 7. Arsenic concentration versus time (initial pH 7, external resistance 20 Ω); (a) iron, (b) magnesium (c) aluminum.

And also based on its characteristics, the highest electronegativity value of iron compared to the other two metals. Iron electronegativity is 1.83, while aluminum and magnesium are 1.5 and 1.3, respectively. Electronegativity is a chemical property that explains the ability of an atom to attract electrons to itself to form covalent bonds.

Based on these results, the research for continuous systems uses iron anode to get the highest arsenite removal efficiency.

3.4 Performance of ACEC reactor with different Hydraulic Retention Time

In the continuous flow experiments, the effect of hydraulic retention time (HRT) on arsenite removal was examined by varying the HRT (4 hour, 8 hour, 12 hour). The initial

pH used was 7, initial arsenite concentration was 3.5 ppm, and the resistance was 20 Ω . From the experiments, it can be seen that hydraulic retention times variation gives effect to arsenite removal. An increase in HRT increased the arsenite removal efficiency. From **Figure 8**, HRT 4, 8, and 12 hour give 42%, 50%, and 99% arsenite removal, respectively. This is due to the longer HRT value or slower inlet flow rate, the higher the formation rate of stable metal hydroxides and the longer the contact time between metal hydroxide and arsenite. It can also enhance the precipitation of the arsenite solution.

Fig. 8. Arsenite removal concentration versus time.

The effects upon power density and electrical current density of HRT variation was also investigated (**Figure 9**). The power density in 12 hour HRT (0.00013 W/m²) was the lowest compared to 8 hour HRT (0.011 W/m²) and 4 hour HRT (0.016 W/m²). It can be concluded from the result that HRT impacts on electricity generation. This phenomenon can be happen because the longer of HRT

and slower inlet flow rate, the lower the arsenite ions concentration to be treated. So, it will decrease the transportation of electron inside the reactor and impact the generation of electricity.

Fig. 9. Power density versus current density for varied HRT 4 hr, 8 hr, 12 hr (Insert : HRT 12 hour).

In recent years, ACEC shows the greatest potential for application in the treatment of arsenic. The comparison of ACEC performance shows in **Table 2**. In previous research, ACEC can remove As(V) up to 99% using the supporting electrolyte. In this experiment, ACEC also proved that it can remove As(III) both in recirculation-batch and continuous flow until 99% even without supporting electrolyte addition using iron anode.

Table 2. Comparison of ACEC technology.

No.	Feed mode	Anode	Capacity (L)	Heavy metal	Operational condition	Duration of treatment (hours)	Power Density (W/m ²)	Removal efficiency (%)	Reference
1	Recirculation	Iron	20	1 L, 1 ppm As (V)	100 mM NaHCO ₃ , pH 5	4	5.9	99.5	[11]
2	Batch	Iron	0.09		60 mM NaHCO ₃ , 50 mL NaCl, pH 5	6	1.99	99.9	[12]
3	Recirculation	Iron	20		10 mM NaCl, pH 7	0.5	0.238	100	[4]
4		Iron	1		10 mM NaCl, pH 7	4	0.18	99.6	[4]
5		Iron	1		10 mM NaCl+10mM Na ₂ SO ₄ , pH 7	8	0.52	100	[4]
6		Aluminium	1		10 mM NaCl, pH 7	4	0.112	99.9	[5]
7		Aluminium	1		10 mM NaCl+8mM Na ₂ SO ₄ , pH 7	24	0.308	98.5	[5]
8	Recirculation	Iron	0.075	2 L, 3.5 ppm As (III)	Without supporting electrolyte, pH 7	24	0.011	99	This study
9		Aluminium	0.075	2 L, 3.5 ppm As (III)		24	0.004	17	This study
10		Magnesium	0.075	2 L, 3.5 ppm As (III)		24	0.103	73	This study

No.	Feed mode	Anode	Capacity (L)	Heavy metal	Operational condition	Duration of treatment (hours)	Power Density (W/m ²)	Removal efficiency (%)	Reference
11	Continuous	Iron	0.075	0.15 L (HRT 12 hr), 3.5 ppm As (III)	Without supporting electrolyte, pH 7	24	0.0013	99	This study

3.5 Anode concentration and pH during arsenite removal process

Anode concentration analysis was used to know the concentration of dissolved metal ions on the solution during the process. Dissolved metal ions were produced due to the oxidation of the anode electrode. The dissolved metal ions then formed stable metal hydroxides and oxyhydroxides in the solution. In general, As(III) removal in ACEC depended on ionic conductivity and the concentration of stable metal hydroxides and oxyhydroxides generated in the solution.

Fig. 10. Anode concentration during the process.

Based on **Figure 10**, iron ions on the solution were the lowest than other metals. Possibly it happens because, iron ions reaction with OH⁻ to form iron- hydroxides was fastest than aluminum and magnesium ions. It also explains the arsenite removal using iron anode was the highest efficiency.

Fig. 11. pH during arsenite removal.

In arsenite removal, pH was a fundamental factor influencing the electrocoagulation process. pH can improve the buffer capacity of the solution. Arsenite and

anode metal ions can exist in a solid form under acidic conditions. Based on **Figure 11**, the pH of iron and aluminum anode was stable around 6-7. The iron's pH constantly decreasing during the process because the OH⁻ ion on the cathode was consumed to produce iron hydroxides with the iron ions.

4 Conclusion

In this study, the ACEC reactor was used for the removal of Arsenite (As³⁺) contained in surface water. The effects of the different anode material and hydraulic retention time (HRT) to the performance of the reactor were investigated. Based on the precipitate analysis, the existence of arsenic was confirmed. The characterization shows that there were magnesium hydroxide and As(V)-O for magnesium-arsenic precipitate and also there were lepidocrocite phase, magnetite (Fe₃O₄), Fe-O, and also As-O bond for iron-arsenic precipitate. Iron has the highest effectiveness (99%) in the arsenite removal process compared to the two other types of metal plates, because it has the lowest solubility constant which can make the metal hydroxides binding with arsenite more easily. However, for electricity production, magnesium is the highest one because magnesium has the lowest potential redox and very reactive so that the highest electrons are produced.

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