A low sludge generated anode by hybrid solar electrocoagulation for the removal of lead

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Abstract In this work, perforated zinc is proposed as a new anode for lead removal by hybrid solar electrocoagulation. The characteristics of the sludge were investigated to understand the behaviour of lead removal during electrocoagulation. Sludge products formed were characterised using X-ray diffraction (XRD), X-ray fluorescence (XRF) and Field Emission Scanning Electron Microscopy (FESEM). In addition, the pH variation during electrocoagulation and effects on the sludge products were examined. At optimum conditions showed that the perforated zinc electrode produced better performance with high removal efficiency, low sludge volume index and less energy consumption.

1. Introduction

Water is vital in human life. It is used in various applications including in agricultural, industrial, shipping, household, recreational, and environmental activities. Hence inadequate infrastructure and management systems for industrial and domestic wastewater have contributed to escalating wastewater crisis, which adversely affects human health [1]. Globally, the total of sewage, agricultural waste, and industrial effluent discharged into the water are about two million tonnes every day [2]. Water polluted by heavy metal ions is extremely harmful to human beings, and it has been a major concern to scientists and engineers around the world.

Lead (Pb(II)) has been extensively documented as one of the most toxic heavy metals. In 2015, it is ranked second in the list of prioritized hazardous substances by The Agency for Toxic Substances and Disease Registry [3]. High concentration of lead in wastewater would harm living organisms and ecosystems. It can damage brain, liver, kidney, basic cellular processes, and reproductive system [4]. Despite these adversities, lead is still a significant contaminant produced in numerous industries such as in the production of batteries, paintings, pigments, fertilizers, cables, alloys, steel, plastics and glass [5, 6]. Based on statistics published by the Statistic Portal, the world’s lead consumption has increased significantly since 2004 [7]. Therefore, it is imperative to reduce lead concentration to an acceptable value before being discharged to the environment. The maximum acceptable limit of lead in drinking water has been outlined by several organisations. The European countries for instance, outlined the limit at 0.01mgL⁻¹. The United States Environmental Protection Agency limited it to 0.015 mgL⁻¹, and the World Health Organization limited it to 0.01 mgL⁻¹ [8, 9]. The Malaysian Department of Environment has set the
allowed level of lead for sewage and industrial effluents for upstream to downstream discharge at 0.1mgL$^{-1}$ and 0.5mgL$^{-1}$ respectively.

Numerous methods have been introduced to remove lead from water and wastewater such as chemical precipitation, adsorption, ion exchange, reverse osmosis, electrochemical, membrane separations, and solvent extraction. Each method has its own advantages and disadvantages [10, 11]. Compared to other alternatives, the electrochemical processes offer several promising approaches for preventing and treating of water polluted by heavy metals. The technique is commended for its versatility, energy efficiency, amenability to automation, environmental compatibility, and cost effectiveness [12, 13]. In an electrochemical process, anode electrodes are dissolved through an electrolysis process to form a range of coagulant species and metal hydroxides [14]. These coagulant species and metal hydroxides are capable of destabilising and adsorbing the dissolved contaminants present in the water or wastewater to be treated [15]. During the process, anodic dissolution of the metal electrodes involves the evolution of hydrogen gas at the cathodes [16]. The hydrogen bubbles then captures and brings aloft any suspended solids formed, before removing the contaminants [17]. There were a few studies conducted to treat the wastewater and synthetic solution containing lead ions involving electrochemical treatment [4, 10, 11, 18-21]. Based on their studies, the most commonly used electrode materials in the electrochemical process were aluminum (Al) and iron (Fe) plate.

Therefore, the main objectives of this study are: (1) to investigate the effect of operating conditions such as interaction between initial-final pH, distance between electrode, sludge volume and energy consumption and (3) to examine the sludge surfaces morphological features by employing the XRD, FESEM surface image and EDAX analysis methods at different pH solution.

2. Materials and methods

2.1. Chemicals

In testing the ion removal for heavy metal, lead nitrate (Pb(NO$_3$)$_2$) was purchased from Sigma-Aldrich Chemical Company. Sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium chloride (NaCl) were bought from Merck. The pH levels of the solutions were adjusted by adding the suitable amounts of 0.01 M H$_2$SO$_4$ or 0.01 M NaOH.

2.2. Electrochemical system set-up

The experiments were conducted by using a 1000 mL borosilicate glass beaker placed on a magnetic stirrer. The electrochemical system was set up with a monopolar configuration. Zinc perforated electrode (dimensions: 7 cm × 5 cm) with hole diameter of 0.5 cm was used as the anode and cathode pairs electrode. The inter-electrode distance was kept constant at 1.0 cm in every experiment conducted. The solar photovoltaic (PV) module (KINVE, KV250-60P) was purchased from BOS Asia Company (Malaysia). The PV panels were fixed to the roof of the Chemical Engineering Department, University of Malaya, Malaysia, located at (3° 7' 1") north latitude and (101° 39' 12") west longitude. The current and voltage of the DC-DC charge controller were within 0–10A and 0–15V ranges, respectively. The pH of the solution was measured by using a pH meter (HANNA instruments). The solution was agitated with a magnetic stirrer at 250 rpm during the process. In addition, 0.01 M of sodium chloride (NaCl) was used as the supporting electrolytes. To determine the system performance, 5 mL samples were taken from the reactor at time intervals of 5 minutes. The samples were later filtered at 0.45 μm to eliminate the sludge formed during the analysis.
2.3. Analytical methods

The residuals of heavy metal concentrations were analysed by Inductively Couple Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin Elmer, Optima 7000 DV). Stock standard solutions (1000 mg/L) for Pb (II) ions were prepared by dissolving lead nitrate Pb(NO$_3$)$_2$ in distilled water. All electrolysis experiments were performed at room temperature and the analyses were carried out in triplicate. Removal efficiency, energy consumption and sludge volume was determined using the following equations [22, 23, 24]:

$$\text{Pb(II) removal (\%) = } \frac{C_o - C_t}{C_o} \times 100$$

(1)

Where $C_o$ is the initial Pb(II) concentration (mg/L) and $C_t$ is the Pb(II) concentration after treatment (mg/L).

$$E \text{ (kWh/m}^3\text{) = } \frac{U \times I \times t}{V}$$

(2)

Where $E$ is the energy consumption (kWh/m$^3$), $U$ is the voltage (V), $I$ is the current (A), $t$ is the treatment time (h) and $V$ is the volume of aqueous solution (m$^3$).

The settleability of the precipitates is indicated by the sludge volume index (SVI), which refers to the volume in millilitres occupied by 1 gram of suspension after 30 min.

$$\text{SVI (mL/g) = } \frac{H_{30}}{H_0 \times SS} \times 1000$$

(3)

Where SVI is the sludge volume index (mL/g), SS is the initial sludge concentration after treatment (g/L), $H_0$ is the initial height of the sludge in the settling column (cm) and $H_{30}$ is the height of the sludge once it has settled after 30 min (cm).

3. Results and discussion

3.1. Effect of pH and treatment time

The initial pH is one of the most sensitive operating parameters influencing the performance of the electrocoagulation process. In order to determine the optimum pH value, a series of batch experiments in the pH range 4.0–9.0 were carried out at a constant initial Pb(II) concentration of 10mg/L, current density of 1.13mA/cm$^2$ and stirring speed of 250 rpm. The effect of different initial pH level on the Pb(II) removal efficiency is shown in Figure 1. Our findings clearly demonstrate that an increase in the pH from 4.0 to 8.0 leads to an increase in the efficiency of Pb(II) removal from 50% to 99% after 20 minutes of treatment. However, the efficiency of Pb(II) removal substantially decreased at pH > 8.0 after 10 minutes of the process. This decrease in removal efficiency at strongly acidic and strongly alkaline pH was due to the amphoteric (at acidic pH) behaviour that leads to soluble cations and monomeric anions (at alkaline pH), in addition, at high pH more sludge was produced this will affect on the performance of Pb(II) removal [19]. The importance of the pH value in the removal of heavy metals from aqueous solutions has been confirmed by Escobar et al. [10], who asserted that the removal efficiency of Pb(II) increased considerably when pH increased. They claimed that, for low pH solutions (i.e. strongly acidic), the oxidation of metal ions diminishes, and therefore the metal removal decreases. At high pH values (i.e.
weakly alkaline), metal removal increased due to the precipitation that occurred in the solution. Figure 2 shows the change of pH after electrocoagulation process. It can be seen that, the final pH for all experiments were higher than initial pH, but for pH 9 the final pH was lower than initial (Figure 2). The results also showed that, sludge volume and energy consumption increased with increasing the pH values. This is because of the enhancement in pH value will cause more sludge was produced and high energy consumption. Selection of optimum pH is important to reduce high operating cost. In our study, the highest Pb(II) removal efficiency was obtained at pH 8, but pH 7 was selected for subsequent experiments due to low energy consumption and sludge volume index (Table 1).

![Figure 1. Effect of pH on the removal of lead by electrocoagulation (initial lead concentration = 10 mg/L, current density = 1.13 mA/cm$^2$, stirring speed = 250 rpm).](image1)

![Figure 2. Effect of pH variation after electrocogulation process (initial lead concentration = 10 mg/L, current density = 1.13 mA/cm$^2$, stirring speed = 250 rpm).](image2)
Table 1. A Comparison of the final pH, sludge production and energy consumption.

| Initial pH | Removal efficiency, % | Sludge volume, mL/g | Energy consumption, (kWh/m³) |
|------------|------------------------|---------------------|-----------------------------|
| 3          | 60                     | 28.5                | 0.192                       |
| 4          | 73                     | 30.8                | 0.202                       |
| 5          | 93                     | 35.2                | 0.216                       |
| 6          | 95                     | 58.5                | 0.230                       |
| 7          | 99                     | 62.5                | 0.249                       |
| 8          | 99.5                   | 68.5                | 0.268                       |
| 9          | 82                     | 71.5                | 0.285                       |

3.2. Characterisation of sludge

Figure 3 presents the XRD analysis of sludge after electrocoagulation treatment. It can be seen that a high peak at 25° to 28° is indicates the presence of zinc oxide. Other compound that which is appears in the image is zinc hydroxide carbonate which show at peak 25° to 28°. Figures 4 and 5 show the EDX and FESEM image, which confirms that, the presence of ultrafine zinc, lead, oxygen and carbon on the electrode surface. This indicates that lead ion has been adsorbed onto zinc oxide.

![Figure 3. XRD image of sludge produced after treatment.](image-url)
Figure 4. EDX image of components in the sludge after electrocoagulation process

Figure 5. FESEM image of components in the sludge after electrocoagulation process
3.3. Effect of electrode distance
To study the effect of the electrode distance on the Pb(II) removal efficiency, several experiments were carried out for varying electrode distances between 0.5, 1.0, 1.5 and 2 cm. When the electrode distance increased, the ohmic loss in relation to the anode and cathode over voltages and the resistance to mass transfer became larger, besides the kinetics of both charge transfer was slowed down [22]. The results also showed that, increase in the electrode distance will decrease removal efficiency. This is due to the rate of particle aggregation and adsorption of Pb(II) became lower. Figure 6 clearly show that the removal efficiency of Pb (II) increased at 0.5-1.5 cm electrode distance and then decreased with the increase of inter-electrode distance. The optimum Pb(II) removal percentage as well as treatment cost was achieved for the electrode distance value of 1.0 cm. Therefore, it was beneficial to choose an optimum small electrode distance of 1.0 cm to minimise energy consumption and increase the Pb(II) removal efficiency.

![Figure 6](image-url)

**Figure 6.** Effect of distance between electrode on the removal of lead by electrocoagulation (initial lead concentration = 10 mg/L, current density = 1.13 mA/cm², stirring speed = 250 rpm).

4. Conclusion
Presence of lead in produced water is one of the reasons that hinder its reusability for other purposes such as irrigation and drinking. The electrocoagulation technique employed in this study is able to reduce the Pb (II) concentration to below the WHO permissible level. Low SVI value was observed by using perforated zinc electrode. Large sludge volume caused longer landfill area usage. Therefore, this electrode was effective in removing Pb (II) with producing low sludge volume and efficient energy consumption. Optimal operating conditions of pH 7.0, current density of 1.13mA/cm², electrode distance of 1.0 cm, initial concentration of 10mg/L and 20 minutes treatment time resulted in 99.1% of Pb (II) removal. The sludge produced containing only zinc oxide, zinc hydroxide and lead oxide. This is indicates that the sludge was not toxic and safe to the environment.
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