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Impulsive removal of Pb(II) at a 3-D reticulated vitreous carbon cathode

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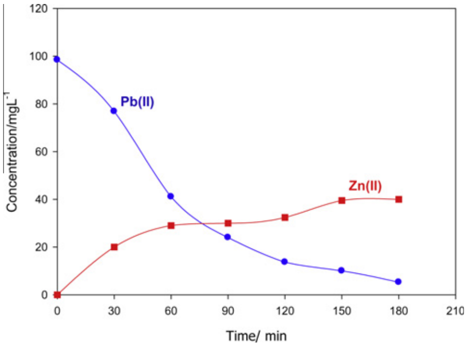
HIGHLIGHTS

- ▶ Spontaneous Pb(II) removal.
- ▶ 73% Cell performance.
- ▶ Catholyte ionic strength of 1.1 is most effective.
- ▶ Pb(II) is deposited in metallic form.

GRAPHICAL ABSTRACT

Because of an impulsive process, the concentration of Pb(II) was decreased and the concentration of Zn(II) was increased with the passage of time.



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ABSTRACT

A batch electrochemical cell was constructed to remove lead(II) ions from aqueous solutions at a 3-D reticulated vitreous carbon (RVC) cathode under acidic pH conditions.

When a RVC cathode was coupled with a Zn anode in the presence of Pb(II) species, an impulsive deposition of lead on the RVC surface occurred with a free energy change of −214.20 kJ mol^{-1} under standard conditions. The system removed 95–99% Pb(II) with a cell performance of 73% under an inert atmosphere. The system exhibited the best performance when the ionic strength of electrolytes was 1.11. The impulsive process was influenced by pH of the medium and dissolved oxygen.

1. Introduction

Lead is a naturally occurring heavy metal found in the earth's crust at about fifteen grams per ton. The metal is widely used for its malleability, density, low melting point, conductivity and resistance to corrosion [1].

The toxicity of lead has been known for a long time and it is the most harmful among the elemental pollutants [2]. Lead poisoning can result from the continued daily intake of lead in amounts as little as 1 mg day^{-1}. Adults who are exposed to lead can suffer from digestive problems, nerve disorders, memory and concentration problems, high blood pressure, hearing problems, muscle and joint pain and reproductive problems [3,4]. In children, lead has a particularly damaging effect on intellectual development. Lead also

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interferes with the manufacture of heme, the oxygen-carrying part of hemoglobin in red blood cells [5].

Lead pollution occurs in many industrial wastewaters such as those produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments and the glass production industry [6]. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of this eventually enter into natural water systems. In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations [5].

There is interest in metal ion removal and metal recovery in order to comply with government legislations on the discharge of wastewater with prescribed levels especially for toxic materials such as heavy metal ions [7]. According to the Malaysian Environmental Quality (Sewage and Industrial Effluents) Regulations 1979, the concentration of lead in effluents for standards A and B must not exceed 0.1 and 0.5 mg L^{-1} respectively [8]. The proposed water treatment by the electrogenerative system is in compliance with this as the lead concentration can be reduced to 0.14 mg L^{-1}.

In these cases, the methods currently being used for heavy metals removal from wastewaters include pH adjustment, chemical oxidation, ion-exchange, electrodialysis and electrochemical reduction [9]. Recoveries of lead metal by crystallization of lead chloride and by cementation with indium strips have been studied from both wastewater and lead-acid battery [10]. Removal of Pb(II) from the wastewater has also been performed with adsorption methods using different adsorbents [11].

Every treatment process has advantages and disadvantages. For example, ion exchange is highly operative in removal of certain charged contaminants; it requires resin regeneration or replacement at a high cost. Ultrafiltration and reverse osmosis are safe processes, but can be prohibitively cost effective. While chemical precipitation is a modest process, it does produce a high volume of secondary sludge [12]. A perfect technology that encounters the requirements of process purity, ease of operation, and low operational costs is the electrogenerative process [13].

In metal removal from dilute aqueous solutions, three-dimensional (3-D) carbon porous materials with properties such as large specific area, high porosity, chemical inertness, good electrical conductivity, good fluid permeability and mechanical resistance, serve as better electrode materials [14].

In this study, Pb(II) removal has been carried out at a 3-D reticulated vitreous carbon (RVC) and porous graphite cathode coupled with a sacrificial Zn anode through an impulsive or electrogenerative process. This process does not require an external supply of energy due to the spontaneous chemical reactions that take place in the reactor which generate an external flow of current as a by-product [15].

The influences of different experimental conditions such as variable Pb(II) concentrations, ionic strength and pH of the catholyte have been studied to remove Pb(II) at the RVC cathode. The morphology of Pb deposits on the cathode has also been investigated.

2. Experimental

2.1. Materials

Lead(II) nitrate, sodium chloride, hydrochloric acid and other chemicals used were of analytical grade supplied by Merck (Germany). The anion exchange membrane used was Neosepta® AM-01 (Tokuyama Corp.). All the solutions were prepared with ultra pure water (resistivity >18 MΩ cm).

2.2. Reactor-batch cell

The schematic diagram of the batch cell is shown in Fig. 1. The cell was made of Plexiglas consisting of two electrolyte compartments having dimensions 5.2 cm × 5.5 cm × 8.0 cm separated by an anion exchange membrane Neosepta® AM-01 (Tokuyama Corp). The separated compartments were treated as cathode and anode chambers, which were filled with solutions of $Pb(NO_3)_2$ and NaCl of known concentrations, respectively. Hence, the anionic exchange membrane was used to avoid inter compartment migration of cations, Pb^{2+} and Zn^{2+}. The galvanic cell components were sandwiched together using eight nuts and bolts. The anode was pure zinc (99% purity) of dimensions 2.0 cm × 4.5 cm × 0.05 cm. The cathode materials used for removal of lead were porous graphite sheet (PG-25) (National Electrical Carbon Products, Inc.) and reticulated vitreous carbon (RVC) 80 porous per inch (ppi) (The Electrosynthesis Co.). The dimensions for the porous graphite PG-25 and RVC 80 ppi electrodes used were 2.0 cm × 4.5 cm × 0.4 cm. The cathodes were cleaned with deionized water and soaked in a mixture of ethanol and water with a ratio of 95:5 for 4 h. The cathodes were then rinsed with sufficient deionized water and soaked in concentrated sulfuric acid for another 4 h. Again, it was rinsed with sufficient deionized water. The treated cathodes were kept in deionized water before being used in experiments. The treatment was needed to remove any impurities on the cathode surface before it was used and to ensure maximum contact between the cathode surface with the solution.

The distance between the electrodes was 2.0 cm and the distance between cathode and anode from the membrane was 1.0 cm each. The electrodes were attached to copper strips, which were used as current collectors. In order to avoid lead deposition onto the current collectors, the metallic surfaces in contact with the solution were covered with Teflon tape. The current collectors were connected with an external conducting wire to complete the circuit.

2.3. Methodology

The detailed experimental conditions are given in Table 1. To start the experiment, 100 mL of 0.5 M NaCl solution was placed in the anode chamber. At the same time, the cathode chamber was filled with 100 mL (10–1000 mg L^{-1}) Pb(II) test solution. Nitrogen gas was used to purge out the dissolved oxygen in both chambers for 30 min and a flux of nitrogen was maintained above the electrolyte surface during the experiment to ensure an inert atmosphere. The spontaneous reaction commenced as soon as the system was short-circuited. The output current and potential of the system were measured with two multimeters (Fluke 77 Series II). During the experiments, 1 mL solution from both anode and cathode chambers, respectively, were collected regularly in order to determine the change in the Zn(II) and Pb(II) concentrations with an atomic absorption spectrometer (AAS) (Perkin Elmer 3100 and Perkin Elmer Analyst 200). The surface morphology of the lead deposits was visualized by scanning electron microscopy (SEM) (Leo Supra 50 VP). Elemental analysis on the deposited cathode surface was carried out by energy dispersive X-ray spectroscopy (EDX) (Oxford INCA 400). Identification and characterization of deposits on the cathode surface were done by X-ray diffraction (XRD) (Siemens D5000). The electrode potentials were determined with respect to the standard hydrogen electrode (SHE).

3. Results and discussion

3.1. Spontaneity of the Pb(II) removal process

An impulsive process goes through a decrease in the system free energy (ΔG^o). In case of an electrochemical process, if the sum of