

Simultaneous removal of acidity and lead from acid lead battery wastewater by aluminum and iron electrocoagulation

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Abstract

In this work the performance of electrocoagulation in the treatment of acid lead battery manufacturing wastewater was studied. Both iron and aluminum sacrificial electrodes remove lead effectively. However, pH of the treated wastewater depends on the electrode material and the supporting electrolyte used. Iron electrocoagulation with KCl as supporting electrolyte reduces the initial Pb^{2+} ion concentration of 8.6 mg L^{-1} to 0.2 mg L^{-1} in 20 minutes of electrolysis time. At the same time, however, the initial wastewater pH of 2.96 rises sharply to 12.24 exceeding by far the upper legal limit for effluent discharge to the environment. On the contrary iron electrocoagulation with Na_2SO_4 as supporting electrolyte does not increase pH sufficiently to the appropriate range. Aluminum treatment with KCl and Na_2SO_4 electrolytes need 35 minutes of electrolysis time for effective lead removal. Effective removal of both, acidity and lead in a single step was achieved in only 25 minutes of electrolysis time with iron electrodes and a mixed supporting electrolyte solution containing $0.03 \text{ M } Na_2SO_4$ and 0.003 M KCl .

Keywords: Acid lead battery wastewater, aluminum and iron sacrificial electrodes, electrochemical coagulation.

1. Introduction

Heavy metal pollution has become in the last decades an increasing environmental problem worldwide. Heavy metals are discharged from various industries, such as mining, metal refineries, smelters, electroplating and textile. Even at low concentrations these metals are toxic to organisms and humans. Lead has long been recognized as one of the three most toxic heavy metals (mercury, lead, cadmium). Therefore, increasing pressure is being placed on industries to reduce their lead wastes. The maximum allowable concentration of lead is 0.05 mg L^{-1} for drinking water and 0.2 mg L^{-1} for effluent discharge. Lead is used for manufacturing of storage batteries, due to its characteristic properties: conductivity, corrosion resistance and reversibility of the reaction between lead, lead oxide and sulfuric acid.

Wastewater from acid lead battery manufacturing or recycling industries contains mainly H_2SO_4 at a pH of 1.2 - 3 and soluble Pb^{2+} ions at a concentration of 5 - 15 mg L^{-1} .

Neutralization with alkaline substances, such as sodium hydroxide, sodium carbonate, lime or dolomite can adjust pH in the appropriate range (5.5 - 9.). This operation, however, cannot effectively reduce the Pb concentration, because the formed $Pb(OH)_2$ is moderately soluble. To

achieve Pb concentrations under the permissible limits a second sulfide or phosphate precipitation or ion exchange is needed. A mixed precipitation/coagulation process based on $Fe(OH)_3$ co-precipitation has been reported by Macchi et al. [1]. When lead ions are removed by ion exchange it is difficult to elude them from the resin by regeneration requiring the disposal of the spent resin. Removal of lead and other heavy metals by biosorption [2], absorption on zeolites [3] membrane electrodialysis [4] and membrane-less electrostatic shielding electrodialysis [5,6], has also been reported.

Chemical coagulation is a quite effective method for treating heavy metal bearing wastewaters but may induce secondary pollution by adding coagulants, such as aluminum or iron salts or organic poly-electrolytes to remove colloidal matter as gelatinous hydroxides. This wastewater treatment process produces large amounts of sludge.

Electrocoagulation uses no chemicals as coagulating agents. These are generated during the electrolysis process by electro-dissolution of a sacrificial anode made of aluminum or iron. Electrocoagulation has been successfully performed for decolorization treatment of dyes and remediation of dye-house wastewaters [7,8], treatment of oil wastes [9,10], dairy effluents [11], diesel and bio-diesel wastewaters [12,13], laundry wastewaters [14], slaughter house effluents [15], arsenic or fluoride containing waters [16,17] and heavy metal bearing effluents [18-21].

In spite of abundant applications of electrocoagulation for the treatment of various kinds of wastewater, its use for the treatment of acid lead battery wastewater is scarce in

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literature [22]. The present work reports the efficiency of electrocoagulation in simultaneously removing both, lead and acidity from battery wastewater in a single operation using electrocoagulation with aluminum and iron electrodes.

2. Materials and Methods

2.1 Chemicals

KCl, Na₂SO₄, H₂SO₄ and KOH were of analytical grade (Merck).

The wastewater sample was obtained from a battery manufacturing unit located near Thessaloniki, northern Greece. Its main characteristics are shown in Table 1.

2.2 Apparatus

A laboratory model DC power supply apparatus (PHYWE Systeme GmbH & Co. KG. Germany) was used to maintain constant DC current. Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (inoLab Cond. Level 1, WTW). The pH and the temperature were measured using a Hanna (HI8314) pH-meter connected to a combined electrode comprising a temperature sensor (HI1217D).

Electrolyses were conducted at room temperature in a cylindrical glass cell of 400 ml in which aliquot solutions of 250 ml were placed and slowly stirred with a magnetic bar at 500 rpm. A pair of commercially obtained aluminum or iron plates of size 10cm x 5cm x 0.5cm immersed to a 6 cm depth with an effective area of 30 cm² each were used as electrodes in the experiments. The inter-electrode distance was 1.5 cm. To remove the oxide and passivation layer from aluminium and iron surface the electrodes were grinded with sandpaper and energized by dipping them in 5N HCl for 1 minute. 0.03 M KCl, 0.03 M Na₂SO₄ or a mixed solution containing 0.03 M Na₂SO₄ and 0.003 M KCl respectively was used as supporting electrolytes. The polarity of the cell was reversed every 20 minutes to limit the formation of the passivation layers on the electrodes.

Samples were extracted every 5 minutes and filtered using Whatman filter paper (Grade 40). The residual Pb concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100). At the end of each experiment the produced sludge and the mass loss of the aluminum electrodes were measured.

Table 1. Main characteristics of wastewater.

Parameter	Value
pH	2.96
Pb (mg L ⁻¹)	8.6
SO ₄ (mg L ⁻¹)	280
Ca (mg L ⁻¹)	76
Mg (mg L ⁻¹)	12

2.3 Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocks inside the wastewater by electrodisolution of soluble anodes made of aluminium or

iron. The main reactions occurring during electrocoagulation produce aluminium ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:



The generated Al³⁺ and OH⁻ ions react to form various monomeric and polymeric species such as Al(OH)²⁺, Al(OH)₂⁺, Al₂(OH)₂⁴⁺, Al(OH)₃⁺, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁷⁺, Al₁₃O₄(OH)₂₄⁷⁺, Al₁₃(OH)₃₄⁵⁺ which finally result in situ formation of gelatinous Al(OH)₃ effecting the coagulation and co-precipitation of particulates from the solution by adsorption as described by Kobya et al. [7]. The liberated H₂ gas at the cathode can remove dissolved organics or any suspended material by flotation. The aluminum hydroxide flocks act as absorbents for heavy metal ions. Furthermore, heavy metal ions combine with the electro-generated OH⁻ ions at the cathode and precipitate in form of their insoluble hydroxides. Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from water.

In case sacrificial iron anodes are used reaction (3) occurs at the anode:



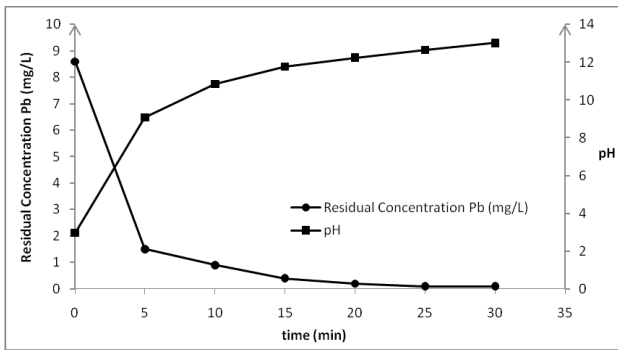
The generated Fe³⁺ ions undergo hydration and give, depending on pH, cationic species such as Fe(OH)²⁺, Fe(OH)₂²⁺ in acidic conditions, neutral Fe(OH)₃ in neutral conditions and anionic species such as Fe(OH)₄⁻, Fe(OH)₆³⁻ in alkaline conditions which finally result in situ formation of gelatinous Fe(OH)₃ effecting the coagulation and co-precipitation from the solution by adsorption. The iron hydroxide flocks act as absorbents for heavy metal ions. Fe³⁺ as a flocculation agent is advantageous, due to its innocuity compared to Al³⁺, which shows some toxic effects.

3. Results and Discussion

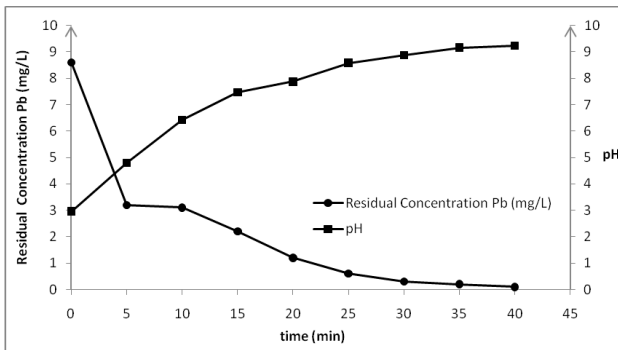
3.1 Treatment with KCl as supporting electrolyte

It is well known that, during the electro-coagulation process, heavy metals are removed by absorption on the electrolytically produced Fe(OH)₃ or Al(OH)₃ flocks and by precipitation in form of their insoluble hydroxides. Furthermore, pH increases, due to hydrogen formation at the cathode. We can take advantage of these phenomena and drive in a single step both, lead concentration reduction under its permissible limit (0.2 mg L⁻¹) and pH elevation to the appropriate range (5.5 – 9). To achieve this, the acid lead battery wastewater was treated electrochemically with iron and aluminum sacrificial electrodes and supporting electrolytes, such as KCl, Na₂SO₄ and a combination of them.

As can be obtained from Fig. 1a the initial Pb concentration of 8.6 mg L⁻¹ falls under the permissible limit in only 20 minutes of electrolysis time with iron electrodes at a current density of 10 mA cm². pH, however, increases sharply to 12.24 exceeding by far the legal limit. When aluminum electrodes are used (Fig. 1b) the reduction of Pb concentration to the legal limit is somehow slower taking 35 minutes whereas pH rises slightly over 9.



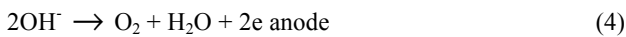
(a)



(b)

Fig. 1. Residual Pb²⁺ ion concentration and pH variation versus time during electrocoagulation of acid battery wastewater with a) iron electrodes and b) aluminum electrodes. (supporting electrolyte KCl 0.03 M, solution volume V = 250 ml, current density i = 10 mA cm²).

Other reactions taking place at the electrodes beyond (1), (2) and (3) are:



Furthermore, the anodically formed Fe²⁺, Fe³⁺ and Al³⁺ ions combine with the cathodically generated OH⁻ ions forming their insoluble hydroxides:



The value of pH rises more sharply when Fe-electrodes are used. Iron has a higher electrochemical potential and therefore higher stability than aluminium. It means that the partial reaction (5) occurs to some extent on cost of reactions (3), (4) and (6). Reaction (5) is more favoured at the more electropositive Fe than at the Al anode. Furthermore, due to considerable difference in solubility between Fe(OH)₂ and Al(OH)₃, the cathodically generated OH⁻ ions are preferentially bound to Al³⁺ than to Fe²⁺ ions. Consequently, a larger excess of OH⁻ ions and a pH increase in the treated solution is observed in case of iron than of aluminium electrocoagulation.

3.2 Treatment with Na₂SO₄ as supporting electrolyte

In absence of Cl⁻ ions and their anodic oxidation reaction (5), pH should not increase sharply, as stated in section 3.1. Fig. 2a shows the electrocoagulation treatment of the battery wastewater with Fe electrodes and Na₂SO₄ instead of KCl as

supporting electrolyte. It can be seen that the residual Pb concentration is brought under the legal limits in 25 minutes of electrolysis time. However, pH increases only slightly to the value of 4.22 which lies under the lower admissible pH limit for effluent discharge to the environment. Replacing Fe with Al electrodes (Fig. 2b) and keeping all other operation parameters unchanged, the residual Pb concentration is effectively removed in 35 minutes. At the same time pH reaches the appropriate value of 5.74. Consequently, with Al electrodes objectives, lead and acidity can simultaneously be removed in a single route. However, the Pb removal takes some more time.

3.3 Treatment with a mixture of Na₂SO₄ and KCl as supporting electrolyte

As the results indicated in sections 3.2 and 3.3 the removal of lead is faster with Fe-electrodes. However, pH either rises sharply exceeding by far the legal limit or it does not increase sufficiently to the appropriate range, dependent on the existence or absence of chloride respectively. It becomes obvious that a small amount of chloride will lead to a moderate increase of pH, so that also it meets the environmental requirement. For this reason a solution mixture containing 0.03 M Na₂SO₄ and only 0.003 M KCl was chosen as supporting electrolyte and the electrocoagulation treatment of the wastewater was repeated with iron (Fig. 3a) and aluminium (Fig. 3b) electrodes and the same rest operational parameters.

It can be obtained from Fig. 3a that with iron electrodes both, lead and acidity are fast and effectively removed in only 25 minutes of electrolysis time. The residual Pb concentration of the battery wastewater diminishes under 0.1 mg L⁻¹ and pH becomes almost neutral reaching the value of 7.88. When using Al-electrodes and keeping all other parameters unchanged (Fig. 3b) the residual Pb concentration diminishes to 0.2 mg L⁻¹ and pH rises to 8.45 in 35 minutes of electrolysis time. Also here lead and acidity are simultaneously removed. The process, however, is somehow slower.

3.4 Electrode mass loss and energy consumption

The costs in wastewater treatment with electrocoagulation are the expenditure on mass loss of electrodes and the electrical energy consumption. The mass loss per liter of the aluminum or iron electrode m_{El} during the wastewater treatment can be calculated from equation (1) using the Faraday's law:

$$m_{El} = \frac{I \cdot t \cdot M}{z \cdot F \cdot V} \quad (1)$$

where V = volume of treated wastewater (L).

Under the operating conditions given the mass loss of the sacrificial aluminum and iron anode for the electrocoagulation of the wastewater with the mixed Na₂SO₄ and KCl supporting electrolyte solution is 2.176010⁻² g Al and 3.218010⁻² g Fe per liter of treated wastewater respectively.

Similarly, the electrical energy consumption E is calculated from equation (2):

$$E = \frac{U \cdot I \cdot t}{V} \quad (2)$$

where U = applied voltage (Volts).

Correspondingly, the energy consumption for aluminum and iron electrocoagulation with the mixed Na_2SO_4 and KCl supporting electrolyte solution amounts to 0.534 and 0.382 Wh per liter of treated wastewater.

3.5 Sludge characteristics

The precipitated sludge was collected, dried at 103°C for 24 h, cooled in a desiccator and weighed. Its amount is determined by the Faraday's law. The electrocoagulation treatment produces apparently lower amounts of sludge compared to the conventional chemical precipitation - coagulation processes.

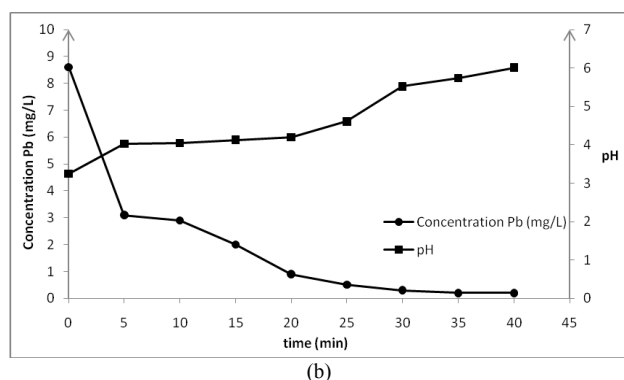
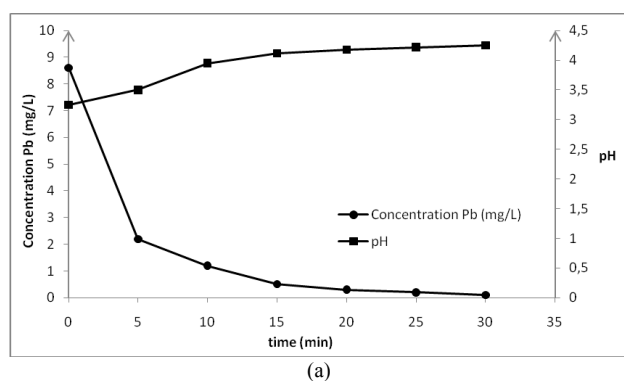


Fig. 2. Residual Pb^{2+} ion concentration and pH variation versus time during electrocoagulation of acid battery wastewater with a) iron electrodes and b) aluminum electrodes. (supporting electrolyte Na_2SO_4 0.03 M, solution volume $V = 250$ ml, current density $i = 10$ mA cm^2).

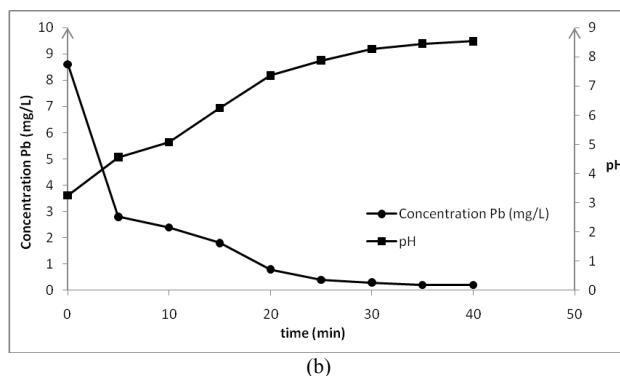
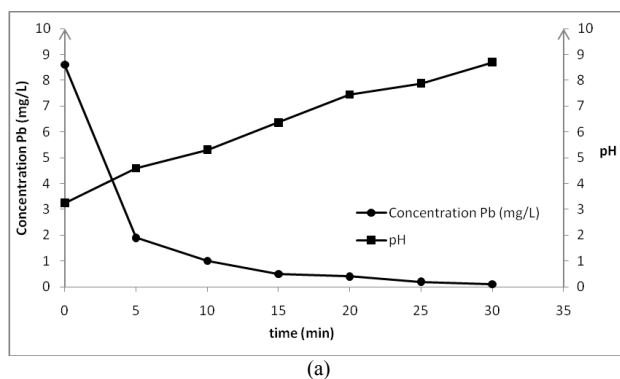


Fig. 3. Residual Pb^{2+} ion concentration and pH variation versus time during electrocoagulation of acid battery wastewater with a) iron electrodes and b) aluminum electrodes. (supporting electrolyte Na_2SO_4 0.03 M + KCl 0.003 M, solution volume $V = 250$ ml, current density $i = 10$ mA cm^2).

4. Conclusions

In this study the applicability of electrocoagulation in the treatment of acid battery manufacturing wastewater for simultaneous removal of both, lead and acidity was investigated. Iron and aluminium sacrificial electrodes and Na_2SO_4 , KCl and a mixture of them as supporting electrolytes were tested and their efficiencies compared. Iron electrodes cause faster removal of lead than aluminium electrodes. Using KCl as supporting electrolyte pH increases sharply exceeding the upper legal limit for effluent discharge to the environment. On the contrary, by replacing KCl with Na_2SO_4 , pH does not increase sufficiently to the permissible range. It was found that best removal efficiency for both, lead and acidity is achieved by using a mixed supporting electrolyte solution containing 0.03 M Na_2SO_4 and 0.003 M KCl.

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