



Electrochemical peroxidation using iron nanoparticles to remove arsenic from copper smelter wastewater



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ABSTRACT

In the present work a study of the electrochemical peroxidation process (ECP) was carried out by using carbon electrodes and iron nanoparticles. Arsenic removal from synthetic and real wastewater from copper pyro-metallurgical industry was analyzed. The experiments were carried out in a 2 L batch reactor with agitation by air injection with airflow of approximately 5 L min^{-1} . A fixed current density of 171.7 A m^{-2} was used and a drop wise 30% (w/w) hydrogen peroxide dosage of around $0.5\text{--}1 \text{ mL min}^{-1}$ was supplied to the wastewater solution. The evaluated operating parameters were: initial pH of the wastewater that was in the range of 2.0 to 6.5 and the treatment time that was varied from 30 to 180 min. The results when the ECP process was applied for 1 h, in the pH range of 2.0 to 6.5, to treat As(III) synthetic wastewater, showed that the maximum removal of arsenic was 62.4% at a pH of 6.5; being approximately constant when more treatment time was applied. On the other hand, when treating As(V) wastewater, the maximum removal was 99.7% at a pH of 5.0. When working with real wastewater in the pH range of 3.5 to 6.5; the arsenic maximum removal was 96% at pH 6.5. This removal was approximately constant when more treatment time was applied. The ECP process using carbon electrodes and iron nanoparticles showed to be a capable technology to remove high concentrations of arsenic (1300 to 3000 mg L^{-1}).

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1. Introduction

Chile is one of the main copper manufacturers in the world [1]. During the processing of the sulphide minerals, in the smelter process, gases that contain sulphur dioxide and arsenic among others are produced; these gases must be cleaned before discharge in the environment. In the copper smelter gas cleaning process, wastewater is produced and it contains high concentrations of arsenic and heavy metals that are far over the Chilean threshold value for discharge in the aquatic environment [2]. At present the wastewater is treated with Ca(OH)_2 , to increase the pH to approximately 10, which favours the precipitation of heavy metals as hydroxides but also precipitates calcium sulphate. Large amounts of arsenic remain soluble in the wastewater and the Ca(OH)_2 addition produces a great volume of sludge, owing to the fact that initial pH of the wastewater is very acidic ($\text{pH} < 1$). This methodology has the disadvantage that great quantity of sludge is produced and requires a subsequent treatment. There are several technologies based on the use of ferric oxides and hydroxides (HFO) that are used to remove heavy metals from wastewater.

These technologies present an alternative to the treatment with Ca(OH)_2 , that at the moment is being applied. The HFO's are highly insoluble precipitates ($K_{\text{sp}} \approx 10^{-38}$) with a large surface area (around $600 \text{ m}^2 \text{ g}^{-1}$). These precipitates are brown–orange colored and have a high affinity to adsorb several heavy metals and therefore are used in wastewater treatments [3–6]. The electrochemical peroxidation process (ECP) is one of the methods that use HFO to remove heavy metals. Until now this process has used steel electrodes and a DC electrical current between them to dissolve the anode and provide the Fe^{+2} that react with the hydrogen peroxide to produce the Fe^{+3} that subsequently results in the HFO production [7–9]. In this work it is proposed to use inert electrodes such as carbon electrodes and iron nanoparticle addition to provide the Fe^{+2} when the Fe^0 is oxidized by the anode process. This could be advantageous over the ECP process when the iron electrodes are dissolved, because from the operational point of view, it would not be necessary to renew the electrodes since the carbon electrodes are not sacrificial. Several differences between the use of steel electrodes with anodic iron dissolution and graphite electrodes with iron nanoparticle addition in ECP are given in Table 1.

Zero valent iron nanoparticles (nZVI), are highly reactive, and they have a large surface area and small particle size, which allow them to remain in suspension [10]. Both iron nano- and

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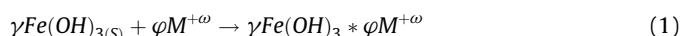
Table 1

Comparison of the use of a) steel electrodes with anodic iron dissolution, and b) graphite electrodes with iron nanoparticle addition when used in ECP.

Parameter	a) Steel electrodes with anodic iron dissolution	b) Graphite electrodes with iron nanoparticle addition.
Passivation of electrodes	Yes	Not observed
Renewal of electrodes during process	Yes	No
Possibility to adapt to fluctuations in arsenic concentration.	Not always. If the current is increased the electrodes could be passivated.	Yes - by adjusting the current density, nanoparticle and/or hydrogen peroxide dosage.
Precipitation of arsenic species at the electrodes.	Yes which increases the electric resistance.	Not observed
Stability of electrode when exposed to air.	Electrode could be oxidized and corrosion could occur.	Yes. It is inert to air.
Necessity to operate ECP process in parallel way.	Yes due to the periodic renewal of the electrodes.	Occasional. For maintenance.
Fragility of electrodes	No	Yes
Possible to use in copper smelter wastewater treatment	Yes	Yes
Final sludge volume	Low	Low
Type of sludge	Mix of ferric arsenate and HFO with metal species adsorbed on surface	Mix of ferric arsenate and HFO with metal species adsorbed on surface
Chemical stability of final solid waste product (from sludge)	Good	Good

microparticles have been suggested for arsenic removal [11]. Because of the significant difference in the specific surface area available for adsorption between microparticles and nanoparticles, the minimum required adsorbent amount per given water volume is much lower in the case of nanoparticles. The iron nanoparticles possess dual properties, because of the dense metallic center enclosed by a thin layer of iron oxide material (FeOOH). The thickness of the outer layer varies from 10 to 20 nm. The oxide layer is an inherent part of the nanoparticles formed instantaneously during their synthesis and responsible for passivation of the metallic center. The oxide layer allows electron passage, conserving the reducing properties of Fe⁰, owing to the fact that the layer is extremely thin and disordered. Furthermore, iron oxides formed from Fe⁰ corrosion are able to oxidize As(III) to As(V). Therefore iron nanoparticles are both able to oxidize and reduce arsenic [12].

This work proposes the HFO formation through the ECP process by the oxidation of iron nanoparticles at the anode and later the oxidation of ferrous ions to ferric ions by hydrogen peroxide. The metal removal occurs due to the formation of HFO followed by an adsorption and/or co-precipitation [9]. The adsorption of heavy metals could be represented as:



When arsenic is present in the aqueous solution, as arsenite, As(III), the hydrogen peroxide oxidizes the arsenite forming arsenate, As(V). The ferric ions react with the arsenate ions and precipitate as ferric arsenate:



This reaction is important when the solution pH is low, (i.e. < 2.5 approximately), because at higher pH value, the main reaction that occurs is HFO formation and later adsorption of the heavy metals.

The objectives of this work were: (i) to establish if the ECP process using iron nanoparticles and carbon electrodes is effective to treat synthetic wastewater containing As(III) and As(V), evaluating the As removal efficiencies, (ii) to establish if the ECP process using iron nanoparticles and carbon electrodes is effective to treat real wastewater from a copper smelter, evaluating the As and Cu removal efficiencies, and (iii) to evaluate the influence of pH and treatment time on the ECP process using iron nanoparticles and carbon electrodes.

2. Experimental

2.1. Reagents

The synthetic wastewater samples were prepared by dissolving either NaAsO₂ or Na₂HAsO₄·7H₂O (both analytical grade) in distilled water. The copper smelter wastewater was sampled from the gas treatment plant at Codelco Chile, División El Teniente, VI Region of Chile. For the pH adjustment, NaOH and 37% (v/v) HCl analytical grade were used.

5 g L⁻¹ NaCl was added to the solutions prepared for the ECP experiments in order to increase the electrical conductivity in the wastewater. 30% (w/w) H₂O₂ was used in ECP experiments. The nZVI were purchased in suspension from the company Nanoiron, the description is showed in Table 2.

Table 2

Characteristic data for the iron nanoparticles.

Product name	NANOFER 25
Generic name	stabilized water dispersion of nanoscale zero-valent iron
Composition	Fe: 14 –18% Fe ₃ O ₄ : 6 –2% C: 0 –1% H ₂ O: 80%
Color	black
Specific gravity	1.15–1.25 g cm ⁻³ (20 °C)
pH	11 – 12
Average particle size	d ₅₀ < 50 nm
Particles specific surface area	> 25 m ² g ⁻¹

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