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Electrocoagulation of arsenic using iron nanoparticles to treat copper mineral processing wastewater

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ABSTRACT

The arsenic content in wastewater is of major concern in copper mineral processing. Typically, a complex wastewater treatment is needed with a combination of chemical and physical processes. Electrocoagulation (EC) has shown its potential for arsenic removal due to the formation of ferric hydroxide-arsenate precipitates but the acidic conditions in the wastewater disfavours the hydroxide formation. This work evaluates the feasibility of EC combined with addition of zero valent iron nanoparticles in the treatment process.

The results showed that copper smelter wastewater could be treated efficiently with EC and presence of nanoparticles. The treatment with EC or nanoparticles alone was less efficient. Increasing the concentration of nanoparticles during EC did not increase the efficiency accordingly. The arsenic removal was favoured by an increase of the current density during EC but only until a limiting current density; thereafter the anodes got partly passivated.

1. Introduction

The pyrometallurgic copper processing releases large amounts of arsenic that vaporize as arsenic trioxide. This compound is absorbed from the gas flow, creating a highly arsenic contaminated acidic wastewater. Typically, a complex wastewater treatment is needed with a combination of chemical and physical processes.

At the sulphuric acid plant connected to the Codelco El Teniente copper smelter, the wastewater treatment can be summarized as shown in Fig. 1 [1]. Indicated on the figure is an initial H_2O_2 oxidation step to oxidize all species – in particular arsenic – in the wastewater. Metals cations such as Cu^{2+} and Zn^{2+} are mainly precipitated as hydroxides during the first precipitation step together with calcium sulphate – but large amounts of arsenic remain soluble in the wastewater. The $Ca(OH)_2$ addition causes an important volume increase – up to 10 times – depending on the initial pH of the wastewater. Combined $Fe_2(SO_4)_3$ and $FeCl_3$ addition in acid deals with the arsenic but since the arsenic concentration in the gas phase changes due to the batchwise operation of the smelter, it is difficult to predict and control the chemical dosage for the precipitation of the arsenic compounds. Typical arsenic concentrations in the wastewater during conventional processing are in the range of 4000–15,000 mg L^{-1} (raw wastewater), 100–1000 mg L^{-1} (after $Ca(OH)_2$ addition) and 0.1–5 mg L^{-1} (after $Fe_2(SO_4)_3/FeCl_3$ addition). Since the Chilean norm for wastewater discharge in rivers is 0.5 mg L^{-1} and the internal Codelco norm for wastewater reuse as process water is 1 mg L^{-1}, in some cases the wastewater has to be recirculated back into the treatment process or reused with a higher content of arsenic. Both these options are undesirable for the copper smelter.

Electrocoagulation (EC) is by now a well known process and has treated a variety of different wastewaters [2–5]. Lately EC has shown to be efficient for arsenic removal from different water streams [6–8]. Hansen et al. [9–11] proposed an airlift EC cell for copper smelter wastewater. It was found that EC could remove arsenic totally from wastewater sampled at (2) and (3) (see Fig. 1) but raw wastewater was difficult to treat with EC – mainly due to the low pH.

On the other hand, several investigations have shown lately that nanosize zero valent iron can precipitate with and/or adsorb arsenic – even at relative low pH [12–16]. Anyway, the iron-to-arsenic (Fe-to-As) molar ratio has to be quite high in order to achieve reasonable arsenic removal rates, and this makes the process expensive.

This work focuses on the combined EC and nanosize zero valent iron treatment of copper smelter wastewater. The objective is to evaluate whether the presence of iron nanoparticles during EC could improve arsenic removal at the acidic pH, considering a Fe-to-As ratio lower than in conventional zero valent iron treatment. The efficiency of the process will be tested for the raw wastewater and wastewater adjusted to pH 2 with $Ca(OH)_2$ in order to remove

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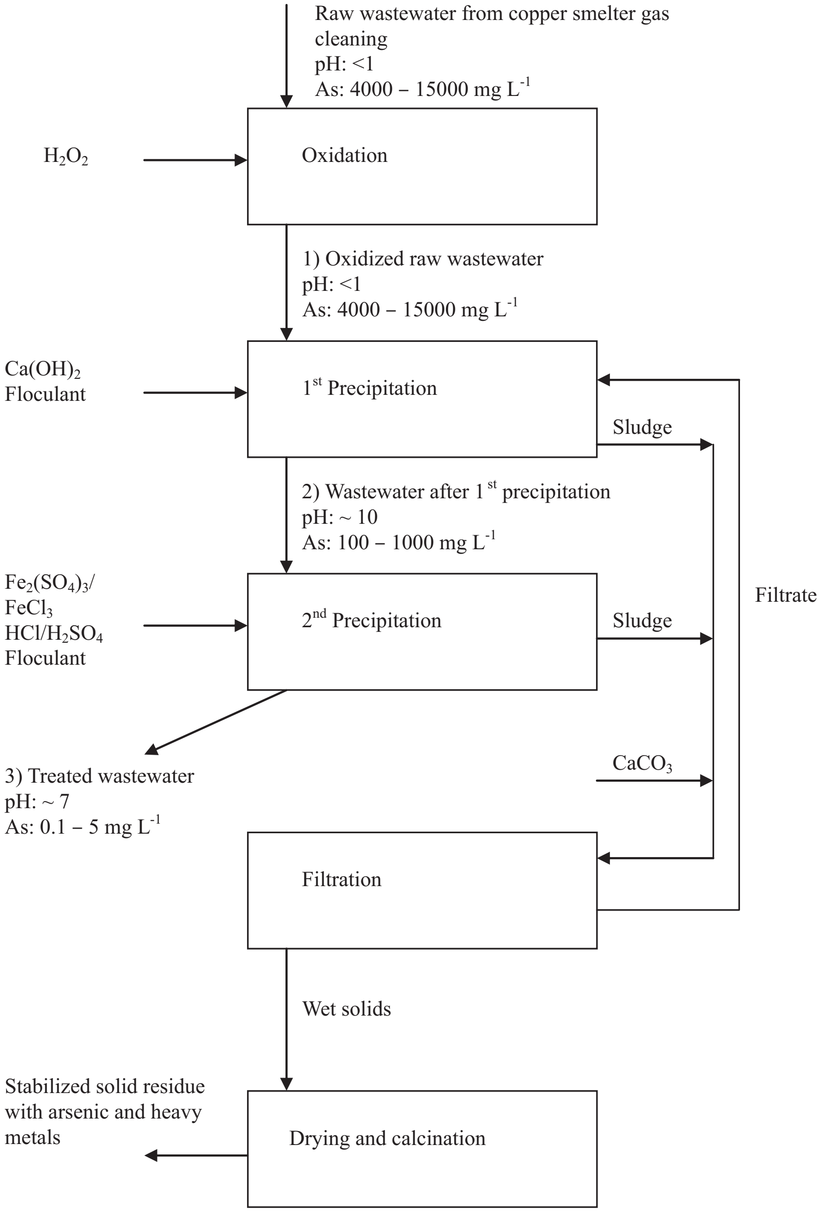

Fig. 1. Actual copper smelter gas cleaning wastewater treatment scheme.

sulphate. Parameters to be analysed are the treatment time, the applied electric current, and the nanoparticle dosage. The results are evaluated in terms of arsenic removal efficiency.

2. Experimental

2.1. Analytical

Before and after the experiments each solution was filtered (paper filter grade 131), and the As content was determined by an Atomic Absorbance Spectrophotometer (AAS) with hydride generation.

pH was measured by standard combination pH electrode connected an ORION, model 370, pH-meter.

2.2. Wastewater characteristics

This work analysed the arsenic removal from two wastewater samples: (1) raw oxidized copper smelter wastewater and (2) wastewater adjusted to pH 2. The first wastewater was sampled at the Codelco El Teniente smelter, VI Region, Chile. The sample was initially measured for As in triplicate. More than 99% of the arsenic was found to be As(V). The total As concentration was measured to 10,290 ± 190 mg L^{-1}, and pH was 0.5 ± 0.2. The second wastewater sample was prepared from the original wastewater applying $Ca(OH)_2$ addition until pH 2. This sample had 2200 ± 50 mg L^{-1} As, and pH was 2.1 ± 0.2.

Wastewater pH adjustment with lime had three purposes:

(1) to favour the presence of negatively charged As(V) species ($H_2AsO_4^-$ and $HAsO_4^{2-}$), which react more rapidly with the different iron species than the uncharged H_3AsO_4, which is the most abundant arsenic species at pH 0.5,
(2) to remove the large amounts of SO_4^{2-} present, precipitating the sulphate with Ca^{2+}. SO_4^{2-} in large amounts would affect the arsenic removal efficiency [17], and
(3) to favour the iron oxy-hydroxide formation, which occurs mainly above pH 1.5–2.