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Elimination of Pb^{2+} through electrocoagulation: Applicability of adsorptive stripping voltammetry for monitoring the lead concentration during its elimination

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ABSTRACT

The aim of this manuscript is to develop a combined method for the detection and remediation of Pb^{2+} species in aqueous environment. The electrocoagulation (EC) process of Pb^{2+} has been studied, using an electrolytic flow cell equipped with Al sacrificial electrodes and by working under galvanostatic conditions (by applying currents of 0.25, 0.5 and 0.75 A). The concentration of Pb^{2+} during EC was monitored by Adsorptive Stripping Voltammetry (AdSV) and data were also confirmed by Atomic Absorption Spectroscopy (AAS). The experimental results of EC showed that the performances of the process slightly depend on the applied current; a complete removal of the pollutant is obtained in all cases, however with different treatment times (90, 75 and 45 min for 0.25, 0.5 and 0.75 A, respectively). Furthermore, the AdSV, when compared with the AAS, has shown that the electroanalytical approach represents a fast and quite reliable alternative for monitoring heavy metal remediation applications.

1. Introduction

In the last decades, heavy metal pollution has become an increasing environmental problem worldwide. Lead (Pb) has long been recognized as one of the three most toxic heavy metals (the other two being mercury and cadmium), however it is widely used for the manufacturing of storage batteries, owing to its unparalleled properties: electrical conductivity, corrosion resistance and reversibility of the reaction between lead, lead (di)oxide and sulfuric acid. The wastewaters from the manufacturing or recycling industries of lead-acid batteries contain high concentrations of Pb and, if not properly disposed of, represent a serious source of pollution to aquatic ecosystems [1].

A traditional physico-chemical treatment for the decontamination of Pb-containing wastewater, prior to their discharge into the environment, is coagulation. It consists in the addition of coagulating agents such as Fe^{3+} or Al^{3+} ions, usually in the form of chlorides, which lead to the formation of flakes that adsorb, entrap, or otherwise bring together suspended matter, thus allowing the subsequent separation of the undesired products. However, this wastewater treatment process produces large amounts of sludge [1,2].

A electrochemical technology that enables similar effects is the electrocoagulation (EC) approach [3–7]. This technique exploits the electric current to dissolve sacrificial anodes based on Fe or Al: when immersed and polarized in the (polluted) water, they give rise to the corresponding metal ions, which may yield to different Fe- or Al-based species, depending on the pH of the medium, as shown in Fig. 1 [5]. These species act as coagulants or destabilization agents, modifying the extent of the electrical double layer of ions or allowing for a charge neutralization, finally leading to heavy metals separation from the wastewater [8,9]. The coagulated particles can be also separated by electroflotation, as they may remain attached to the bubbles of H_2 gas evolved at the cathodes and can be transported to the top of the solution, from where they are easily removed. Generally speaking, the EC approach has the interesting characteristics collected in Table 1 [5].

Electrocoagulation has been successfully exploited for the decontamination of several kinds of wastewater, such as effluents containing dyes, treatment of oil wastes, diary effluents, diesel and bio-diesel wastewater, laundry discharges and slaughter house wastes [10–24].

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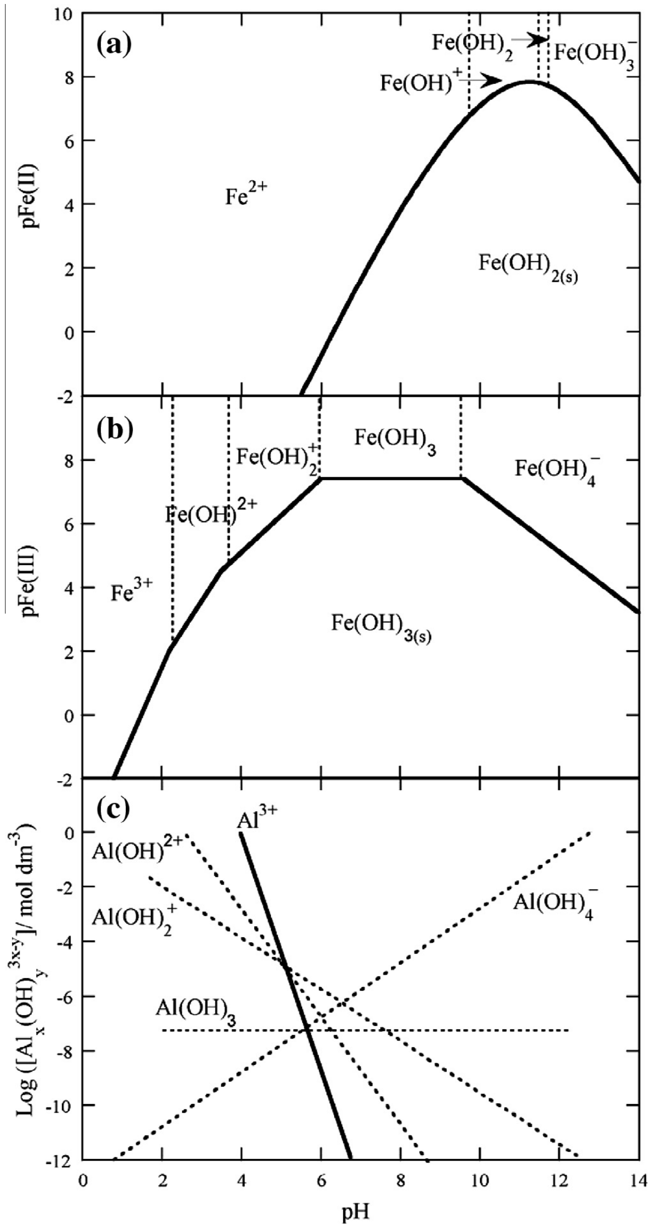

Fig. 1. Predominance-zone diagrams for (a) Fe(II) and (b) Fe(III) chemical species in aqueous solution; the straight lines represent the solubility equilibrium for insoluble $Fe(OH)_2$ and $Fe(OH)_3$, respectively, and the dotted lines represent the predominance limits between soluble chemical species. (c) Diagram of solubility of Al(III) species as a function of pH. Adapted from Ref. [5].

In the case of heavy metals removal, the residual concentration of pollutants is frequently determined by using the Atomic Absorption Spectroscopy (AAS); however, this analytical method is expensive (from the point of view of equipment acquisition) and also involves toxic or costly reagents [12,15–18,21–23]. In last decades, electroanalysis has attracted considerable interest as an alternative way for detecting, quantifying and monitoring the concentration of different heavy metals; actually, these electrochemical methods offer high sensitivity and selectivity [25–31]. Although the use of these techniques, to quantify both organic and inorganic species, does not present particular limitations, only a few studies have appeared on their utilization in combination with electrochemical reclamation technologies (typical methods like electrocoagulation, electrochemical reduction, direct or indirect electrochemical oxidation, or emerging electrochemical “advanced oxidation processes” such as electro-Fenton, photoelectro-Fenton and photoelectrocatalysis [5]), for monitoring the pollutants (organic compounds, heavy metals, and gas products.) during their elimination.

For example, an analytical procedure based on square wave voltammetry has been recently proposed by Cesarino et al. [32] for the real time monitoring of the phenolic compounds that get formed during the electrolysis of benzene, and obtained results were shown to fully agree with those achieved by HPLC. The applicability of electroanalytical techniques was also demonstrated for monitoring the concentration of oxalic acid (OA) during its electrochemical oxidation (EO) in acidic media at boron doped diamond (BDD) electrodes [33], as well as on other electrocatalytic materials [34]. In the latter investigations, differential pulse voltammetry (DPV) measurements were carried out, and both the calibration curve approach and the standard addition method have allowed to attain a good fit, confidence intervals and limits when compared with HPLC analyses.

Therefore, in the present work, attention has been focused on the electrocoagulation (EC) of Pb^{2+}, with a double purpose: (i) to identify the influence of the applied current on the electrochemical elimination of the heavy metal, and (ii) to verify the applicability of an electroanalytical technique (the Adsorptive Stripping Voltammetry (AdSV), carried out at a glassy carbon electrode) for the monitoring of the Pb^{2+} concentration during its elimination by means of electrocoagulation.

2. Experimental

2.1. Reagents

Two stock solutions of Pb^{2+} were prepared in 0.5 mol L^{-1} $NaNO_3$, using MilliQ water: the first one (50 mg L^{-1}) was used as the standard solution for electroanalysis tests and calibrations, while the second (300 mg L^{-1}) was employed as model waste in the electrocoagulation experiments. All chemicals were of analytical grade and supplied by Vetec Company.

2.2. Analytical methods

During the EC tests, the Pb concentration was determined through measurements with both, AdSV and AAS. The electrochemical analyses were carried out using an Autolab model PGSTAT320N; experiments were carried out in a conventional three-electrode system, and measurements were performed between −1.2 and 0 V, in 0.5 mol L^{-1} $NaNO_3$ at 25 °C. A GC electrode with an exposed geometric area of ca. 0.5 mm^2 was used as the working electrode, while a platinum wire and an Ag/AgCl (KCl 3 mol L^{-1}) were employed as the auxiliary and reference electrodes, respectively. The other details of the procedure were as follows: potential scan rate of 50 mV s^{-1}; equilibration time: 10 s; pre-concentration time: 30 s; modulation time: 0.04 s; step potential: 0.006 V; modulation amplitude: 0.05 V; standby potential: 0.05 V.

In order to determine the Pb concentration in the samples that were collected during EC processes, a calibration curve for Pb^{2+} was obtained by evaluating the AdSV peak intensity as a function of analyte concentration, and considering at least twelve different analyte concentrations. However, it is important to remark that, during EC experiments, the concentration of collected samples was superior to the linear concentration range obtained by AdSV, for this reason, an electrolysis sample (0.5–1 mL) was put in 30 mL of supporting electrolyte, after that, by adding known volumes of the Pb^{2+} solution in the measuring vessel, the concentration of Pb^{2+} in the solution was quantified under experimental conditions described above. The lead concentration was also