



# Potentiometric electronic tongue-flow injection analysis system for the monitoring of heavy metal biosorption processes

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## ABSTRACT

An automated flow injection potentiometric (FIP) system with electronic tongue detection (ET) is used for the monitoring of biosorption processes of heavy metals on vegetable wastes. Grape stalk wastes are used as biosorbent to remove  $\text{Cu}^{2+}$  ions in a fixed-bed column configuration. The ET is formed by a 5-sensor array with  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$ -selective electrodes and electrodes with generic response to heavy-metals, plus an artificial neural network response model of the sensor's cross-response. The real-time monitoring of both the  $\text{Cu}^{2+}$  and the cation exchanged and released ( $\text{Ca}^{2+}$ ) in the effluent solution is performed by using flow-injection potentiometric electronic tongue system. The coupling of the electronic tongue with automation features of the flow-injection system allows us to accurately characterize the  $\text{Cu}^{2+}$  ion-biosorption process, through obtaining its breakthrough curves, and the profile of the  $\text{Ca}^{2+}$  ion release. In parallel, fractions of the extract solution are analysed by spectroscopic techniques in order to validate the results obtained with the reported methodology. The sorption performance of grape stalks is also evaluated by means of well-established sorption models.

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## 1. Introduction

The toxic effects of heavy metals in the environment are well known and governments introduce strict regulations with regard to metal discharge, mainly from industrial processes. Toxic metals are not easily biodegraded and enter in the food-chain where they can be accumulated on living tissues causing serious diseases. For these reasons, it becomes necessary to remove them from liquid wastes at least to the limit accepted by the regulations. The elimination of heavy metals in aqueous effluents frequently requires the use of complex and expensive technologies [1,2].

Recently, the ability of biological materials to fix metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater heavy metal removal. These materials represent a suitable alternative as compared to conventional sorbents frequently used (ion-exchange resins, activated carbon, etc.). Specially, their low cost makes their disposal feasible in contrast with an expensive regeneration. One of these sorbents, grape stalk wastes generated in the wine production process, resulted in a good sorption system for the elimination and

recovery of metal ions as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr(VI)}$  and  $\text{Cr}^{3+}$ . These studies have been carried out at laboratory scale, in both batch and continuous-flow methodologies [1–4].

First results obtained in batch experiments indicated that the sorption of heavy metals on grape stalks released alkaline and alkaline earth metals ( $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), as well as protons [5], suggesting that ionic exchange is predominantly responsible for metal ion uptake.

Conventionally, analytical methods as flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and flow injection analysis with potentiometric detection (FIP) have been used in the monitoring of metal biosorption processes. The advantages of these methods are well known, however there are several drawbacks to consider: the spectroscopic methods use expensive equipment, are not well suited to on-line operation, require trained personal and, in many cases, a sample treatment is needed, affecting the analysis time. On the other hand, FIP is much user-friendly, produces data ideally at real time, permits automation and has a high sampling throughput. However, FIP depends of the quality and selectivity of the ion-selective electrodes used. Moreover, methods above may present some limitations on simultaneous or multiparametric analysis, an important aspect when working with real samples.

In the last years, the sensor's field has attempted the simultaneous analysis of species with a new strategy based on the use of multiple sensors showing cross-selectivity, in the approach known

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as electronic tongue (ET). According to the recent IUPAC definition [6] an ET is a “multisensor system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on pattern recognition and/or multivariate data analysis—artificial neural networks (ANNs), principal component analysis (PCA), etc”. The purpose of the processing tool differs depending on the application; it can be to identify a chemical species or to determine its concentration without having to eliminate interferences or to quantify them at all [7].

Considering the number of works already published and the number of different laboratories working with their principles, electronic tongues and electronic noses, bio-inspired sensor analysis systems for liquid and gas determination respectively, can be qualified as a consolidated trend in the sensor's field, [8,9]. The applications of ET systems found in the literature are extended, especially for qualitative analysis (recognition, identification, classification) [7,10,11], even though quantitative analysis is becoming more important in the last few years [12,13], especially the resolution of multicomponent mixtures [14]. Thanks to these range of possibilities, ETs are starting to prove useful as quality control devices in the food industry/environment along with a few other applications such as water and process monitoring and clinical analysis [7]. The application of ETs in the simultaneous multi determination of heavy metals was successfully demonstrated in mine leachates [15], as well as more recently, in environmental field by using a light addressable potentiometric sensor (LAPS), prepared in an array format and furnished with differentiated selectivity chalcogenide thin films [16].

Sensor arrays have been integrated frequently in flow systems in order to automate the sample handling and the recording of the multichannel signals [7]. A recent review inspected in detail the use of electronic tongues as detection systems in flow systems, specifically by using flow injection analysis (FIA) principles as automation aid [17]. In these terms, a FIA system employing an array of chalcogenide glass sensors was described with the aim of determining heavy metals [18].

In the present work, the removal of  $\text{Cu}^{2+}$  ions from aqueous solutions onto grape stalk wastes in a fixed bed column is evaluated. The real-time monitoring of both the  $\text{Cu}^{2+}$  and the cation exchanged and released ( $\text{Ca}^{2+}$ ) in the effluent solution is performed by potentiometric sensors by combining flow-injection techniques (FIP) and electronic tongue (ET) detection. Flow-injection potentiometric electronic tongues (ET-FIP) are a novel trend in the sensor field [7] in which the implementation of sensor arrays and FIP generates complex response peaks that can be processed with chemometric tools as a procedure to solve complex mixtures from chemical process analysis as, per example, metal biosorption from polluted effluents; the ET-FIP approach is intended for improving the performance of single sensor detection.

## 2. Materials and methods

### 2.1. Reagents and materials

The ionophores, calcium bis[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-phosphate (CaBTMBPP), calcium-ionophore I (ETH 1001), tetrabenzyl pyrophosphate (TBPP), [2,2']-furdioxime monohydrate (FDMH); the plasticizers, dioctylphenylphosphonate (DOPP), 2-nitrophenyloctylether (NPOE), bis(1-butylpentyl)adipate (BBPA), dibutylphthalate (DBP); the additives, sodium tetratheryborate (NaTPB) and potassium tetrakis(4-chlorophenyl)borate (KTpCIPB); and the polymer chromatographic grade poly(vinyl chloride) (PVC) were purchased from Fluka (Buchs, Switzerland).

Metal solutions were prepared by dissolving appropriate amounts of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$  or  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$  in deionised water (Milli-Q, Millipore; Molsheim, France). These reagents, tetrahydrofuran (THF) and metal standard solutions ( $1000 \text{ mg L}^{-1}$ , used for Flame Atomic Absorption Spectroscopy, FAAS) were analytical grade and purchased from Merck (Darmstadt, Germany).

Grape stalk wastes generated in the wine production process (supplied by a wine manufacturer of Subirats, Penedès DO region, Barcelona, Spain), were rinsed three times with deionised water, dried in an oven at  $110^\circ\text{C}$  until constant weight, and finally cut and sieved for a particle size of 0.8–1.0 mm. Their properties as sorbents are in Ref. [19].

### 2.2. Membranes and electrodes

The ion-selective electrodes (ISEs) employed in the electronic tongue were all-solid-state tubular flow-through electrodes. Heterogeneous membranes based on a composite of  $\text{Ag}_2\text{S}$ – $\text{CuS}$  in epoxy resin were used in the preparation of the  $\text{Cu}^{2+}$ -selective sensors as is reported in the literature [19]. The  $\text{Ca}^{2+}$ -selective and the two generic sensors were prepared by using the corresponding ionophore in a PVC membrane, and constructed according to established procedures in our laboratories [20]. The composition of the sensor membranes used in the ET is listed in Table 1. All the flow-through tubular electrodes were placed inside a Perspex sandwich module, for their insertion in the flow system [26]. An Orion double-junction electrode (Model 90-02-00, Thermo Fisher Scientific, Beverly, MA, USA) was used as reference electrode.

### 2.3. Sorption experiments

All sorption experiments were conducted in duplicate in glass columns of 72 mm length and 10 mm internal diameter (Omnifit) and uniformly packed with 1.3 g of grape stalk waste (particle size of 0.8–1.0 mm) previously treated. During the column sorption operation, the aqueous metal solution containing approximately  $35 \text{ mg L}^{-1}$  of  $\text{Cu}^{2+}$  was pumped upwards through the column at a constant flow rate ( $30 \text{ mL h}^{-1}$ ). The sorption of  $\text{Cu}^{2+}$  ions from this solution involves ion-exchange processes where  $\text{Ca}^{2+}$  present in the grape stalk, are released. The influent solution in the column sorption consist in the solution of  $\text{Cu}^{2+}$  ion in deionised water, the effluent outlet of the column is composed by a variable content of calcium released from biosorbent as well as other ions ( $\text{H}^+$ ,  $\text{K}^+$ , etc.) in lower amounts. The column effluent is pumped in fixed time intervals to the sensor array, which determines the concentration of calcium and copper in time. In order to compare with conventional analytical techniques, samples were collected from the outlet of the column by a fraction collector (Gilson FC204) at pre-set time intervals. Afterwards, metal concentrations in the influent and effluent solution were determined by flame atomic absorption spectrometry (FAAS, at a wavelength of 324.8 nm) using a Varian absorption spectrometer (Model 1275) and by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer model Optima 4300DV) for  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$ , respectively. All experiments were performed at room temperature.

### 2.4. Breakthrough sorption capacity

The capacity at exhaustion  $q_{\text{column}}$  ( $\text{mmol g}^{-1}$ ) is determined by calculating the total area below the breakthrough curve. This area represents the amount of solute sorbed by mass of solid in the sorption zone that goes from the breakpoint to exhaustion [3,4].

The breakthrough point is chosen arbitrarily at some low value,  $C_b$  ( $\text{mmol L}^{-1}$ ); and the sorbent is considered to be essentially

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