Simultaneous and automated monitoring of the multimetal biosorption processes by potentiometric sensor array and artificial neural network

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ABSTRACT

In this communication, a new methodology for the simultaneous and automated monitoring of biosorption processes of multimetal mixtures of polluting heavy metals on vegetable wastes based on flow-injection potentiometry (FIP) and electronic tongue detection (ET) is presented. A fixed-bed column filled with grape stalks from wine industry wastes is used as the biosorption setup to remove the metal mixtures from the influent solution. The monitoring system consists in a computer controlled-FIP prototype with the ET based on an array of 9 flow-through ion-selective electrodes and electrodes with generic response to divalent ions placed in series, plus an artificial neural network response model. The cross-response to Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+} and Ca^{2+} (as target ions) is used, and only when dynamic treatment of the kinetic components of the transient signal is incorporated, a correct operation of the system is achieved. For this purpose, the FIA peaks are transformed via use of Fourier treatment, and selected coefficients are used to feed an artificial neural network response model. Real-time monitoring of different binary (Cu^{2+}/ Pb^{2+}), (Cu^{2+}/ Zn^{2+}) and ternary mixtures (Cu^{2+}/ Pb^{2+}/ Zn^{2+}), (Cu^{2+}/ Zn^{2+}/ Cd^{2+}), simultaneous to the release of Ca^{2+} in the effluent solution, are achieved satisfactorily using the reported system, obtaining the corresponding breakthrough curves, and showing the ion-exchange mechanism among the different metals. Analytical performance is verified against conventional spectroscopic techniques, with good concordance of the obtained breakthrough curves and modeled adsorption parameters.

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1. Introduction

Heavy metals are one of the most harmful pollutants to different ecosystems and human health. Therefore they require special attention, both control and treatment of heavy metals in different waste leads to use of expensive and complex methodologies [1,2].

Our group has studied the biological materials as bio-accumulators of heavy metals. The grape stalks generated from wine industrial wastes have taken a key role in this sense. In recent years, several works have demonstrated the ability of grape stalk wastes as good sorption material for the removal and recovery of metal ions, such as: Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Cr(VI) and Cr^{3+} [3–5]. Previous experiments in fixed-bed column configuration indicated that the sorption of heavy metals on grape stalks released alkaline and alkaline earth metals (K^+, Mg^{2+}, Ca^{2+}), as

well as protons [6], suggesting that ionic exchange is predominantly responsible for metal ion uptake.

In the monitoring of metal biosorption processes, conventional analytical methods have been traditionally used, as flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and flow injection analysis with potentiometric detection (FIP) [7]. However, the limitations of these methods, the need to seek new alternatives adaptable to the study of more complex processes, specifically in multimetal mixtures and in unconventional circumstances, have led us to consider other viable alternatives such as detection with the use of sensor arrays, or electronic tongues (ET) [6].

Considering an ET as a multisensor system combined with advanced mathematical procedures for signal processing [8], the purpose of the latter differs depending on the application. If the goal is qualitative, Principal Component Analysis (PCA) is the most commonly used method, to visualize if the samples can be separated in classes (classified), or to identify a specific variety [9–11]. When the purpose is a quantitative analysis, different tools may be used; these include: principal component regression (PCR), partial least squares (PLS) or Artificial Neural Networks (ANNs) [11–14].

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The greatest advantage of using a sensor array is its ability to generate multivariate analytical data in real time and simultaneously to permit tackling the identification of interferents and the compensation of matrix effects [15]. These advantages have provided ETs with encouraging results in the monitoring of numerous processes, viz. in the industrial, clinical and environmental fields, especially in the resolution of multicomponent mixtures [15,16]. Several works of these applications stand out in the literature; Gutiérrez et al. used a sensor array formed by potentiometric sensors for the monitoring of NH_4^+, K^+, NO_3^- nutrients and Na^+, Cl^- contaminants in a fertigation solution for greenhouse cultivation [17]. Other applications associated to farming activities can be found in the work by Chang et al., related to the monitoring of water quality in fish farms which employed a screen-printed electronic tongue formed by 8 potentiometric sensors [18]. Multisensor arrays have been used as electronic tongues in the classification of mineral waters [19]. However, there are few references where an electronic tongue has been employed for simultaneous quantification of different metal ions in liquid samples [20]. Even though several authors in different types of samples have demonstrated the determination of trace heavy metals using ETs, [21,22] their use in the simultaneous monitoring and discrimination of heavy metal mixtures in industrial processes is scarce.

By integrating a flow analysis system with an electronic tongue, obvious advantages can be seen: as among others, automation, simultaneous determination and analysis in series. Several researchers have reported work leveraging this valuable tool [6,22–24]. Especially, dynamic components of the sensors' signal can be exploited and incorporated in the data treatment to help achieving a better performance from the ET system [13].

The final goal of this work is to develop a fully-automated system and analytical methodology for the simultaneous and real-time determination of heavy metals considered to be pollutants in environmental samples, employed during their removal and recovery via biosorption processes. Considering the complexity of the multimetal samples, as well as the effluent media, the combination of flow-injection techniques and electronic tongue detection (ET–FIP) is considered to be a satisfactory approach for the final objective of the monitoring of a biosorption process. Thus, biosorption of binary and ternary mixtures of divalent heavy metals using grape stalk wastes as the sorbent material implemented in a laboratory-scale fixed bed column is evaluated.

The real-time monitoring of the trace metals exchanged and the released ion (Ca^{2+}) in the effluent solution was therefore achieved by a potentiometric sensor array in conjunction with the ET–FIP system. Multidimensional transient information obtained from the flow-injection potentiometric electronic tongue system was treated with advanced chemometric tools such as an ANN, and methods of signal pre-processing such as the Fourier transform, with the ultimate goal of characterizing sorption properties against mixtures of heavy metals.

2. Experimental

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), 1,3-bis(N-benzoylthioureido) benzene (BTB), S,S´-methylene bis(N,N-diisobutyldithiocarbamate) (MBDiBDTC), cadmium-ionophore I (N,N,N',N'-tetrabutyl-3,6-dioxaoctanedi(thioamide), TBDTA, trioctyl phosphine oxide (TOPO) and tetrabutyl thiuram disulfide (TBTDS); the plasticizers, dioctylphenylphosphonate (DOPP), 2-nitrophenyloctylether (NPOE), bis (1-butylpentyl)adipate (BBPA), (10-hydroxydecyl)butyrate (ETH 264) and dioctyl sebacate (DOS); the additive potassium tetrakis (4-chlorophenyl)borate (KTpClPB); and the polymer grade poly (vinyl chloride) (PVC) were obtained from Fluka (Buchs, Switzerland).

Stock metal solutions were prepared by dissolving appropriate amounts of their nitrate salts in deionised water (Milli-Q, Millipore; Molsheim, France). These reagents, tetrahydrofuran (THF) and metal standard solutions (1000 mg L^{-1}, used for Flame Atomic Absorption Spectroscopy, FAAS) were analytical grade and purchased from Merck (Darmstadt, Germany).

Grape stalk wastes (supplied by a wine manufacturer of Subirats, Penedès DO region, Barcelona, Spain), were rinsed and treated as in previous work [7]. A particle size of 0.8–1.0 mm was used in all experiments.

2.2. Membranes and electrodes

The tubular flow-through electrodes (ISEs) used in the ET–FIP system corresponded to all-solid-state type or non-symmetric configuration; these electrodes are based on a direct ohmic contact between the transducer and the membrane. Two types of membranes were used: heterogeneous crystalline membranes, based on a composite of Ag_2S–CuS in epoxy resin used in the preparation of the Cu^{2+}-selective sensors [7], and polymeric membrane with mobile carrier, constructed according to established procedures in our laboratories [25]. Table 1 shows the composition of the membranes used in the sensors arrays [26–33]. The ISEs were inserted in the flow system with help of a Perspex sandwich module [34]. The potentiometric measurement cell was

Table 1
Composition of the sensor membranes employed in ET–FIP.

Sensor	PVC (%)	Plasticizer (%)	Ionophore (%)	Reference
Ca^{2+} (1)	33.3	NPOE (65.2)	Calcium-ionophore I (1.0)	[23]
Ca^{2+} (2)	29.8	DOPP (63.2)	Calcium bis[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-phosphate (7.0)	[24]
Pb^{2+} (1)	37.2	NPOE (49.6)	S,S´Methylenebis(N,N-diisobutyldithiocarbamate) (11.2)	[25]
Pb^{2+} (2)[a]	33.0	DOS (61.5)	1,3-bis(N-benzoylthioureido)benzene (5.0)[b]	[26]
Zn^{2+}	40.2	NPOE (53.6)	Tetrabutyl thiuram disulfide (5.3)[b]	[27]
Cd^{2+}	34.0	ETH 264 (65.0)	Cadmium-ionophore I (1.0)[b]	[28]
Generic (1)	34.5	BBPA (63.2)	Tetrabenzyl pyrophosphate (2.3)[b]	[29]
Generic (2)	37.7	NPOE (54.9)	Trioctyl phosphine oxide (5.2)[b]	–
Cu^{2+}	CuS (30.9%), Ag_2S (30.9%), Araldite M (27.2%) and HR hardener (10.9%)			[30]

[a] Ionophore not commercially available.
[b] The formulation included potassium tetrakis(4-clorophenyl)borate as additive.