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# Simultaneous electrochemical sensing of emerging organic contaminants in full-scale sewage treatment plants

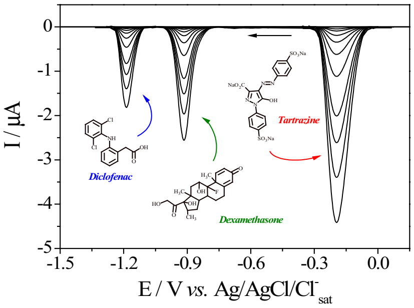
Thiago Mielle B.F. Oliveira [a,b,*], Germana de P. Pessoa [c], André B. dos Santos [c], Pedro de Lima-Neto [b], Adriana N. Correia [b]

[a] Departamento de Química, Universidade do Estado do Rio Grande do Norte, Campus Central, Setor II, 59625-620 Mossoró, RN, Brazil
[b] Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Bloco 940, Campus do Pici, 60455-970 Fortaleza, CE, Brazil
[c] Departamento de Engenharia Hidráulica e Ambiental, Universidade Federal do Ceará, Campus do Pici, 60455-900 Fortaleza, CE, Brazil

## HIGHLIGHTS

- Hg-sensors had unique properties for the electroanalysis of organic contaminants.
- Traces of tartrazine, dexamethasone and diclofenac were simultaneously analyzed.
- Analytical sensing was enhanced by coupling voltammetric and extraction techniques.
- The proposed method was suitable to analyze the target compounds in wastewaters.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein, a highly sensitive and selective simultaneous electrochemical method to monitor the emerging organic contaminants tartrazine (TRT), dexamethasone (DMZ) and diclofenac (DCL) in sewage treatment plants was developed. The sensing was based on electroreduction of TRT (−0.22 V), DMZ (−0.93 V) and DCL (−1.12 V) on hanging mercury drop electrode (HMDE), using citrate buffer pH 2.5 as electrolyte. The fast electrodic kinetics of these chemicals provided improvements on selectivity at high scan rates. The unique electrochemical properties of HMDE were associated to analytical performance of the square-wave voltammetry to quantify trace concentrations of TRT, DMZ and DCL, with detection limits ranging from $2.78 \times 10^{-8}$ to $1.48 \times 10^{-7}$ mol $L^{-1}$. After wastewater treatment by using solid-phase extraction, the proposed procedure was successfully applied for the direct quantification of the studied compounds with high precision, accuracy and stability of the measurements, even in the presence of other electroactive contaminants.

## 1. Introduction

Brazil has faced serious pollution problems with its water resources, thus representing environmental and public health concerns [1,2]. Sewage discharge has been highlighted as the most important pollution source, in which it tends to become worse in the areas that have intermittent rivers or surface waters with a low dilution capacity, as seen in semi-arid regions. For instance, the Ceará state has one of the highest population densities in the Northeast (*c.a.* 60 people per $km^2$), but unfortunately the sanitized areas are still quite limited. The wastewater produced are generally treated by biological processes, with emphasis on stabilization ponds (62%), which along with the upflow anaerobic sludge

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* Corresponding author at: Departamento de Química, Universidade do Estado do Rio Grande do Norte, Campus Central, Setor II, 59625-620 Mossoró, RN, Brazil. Tel.: +55 84 3315 3011; fax: +55 84 3315 2235.

*E-mail address:* dr.thiagomielle@gmail.com (T.M.B.F. Oliveira).

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blanket reactors, it represents the sewage treatment process mostly used in the country. However, recent studies verified the inefficiency of the pound technology to remove important bioactive compounds, namely emerging organic contaminants (EOCs), which compromise the quality of the receiving waters [1]. EOCs are natural or synthetic substances that are not commonly monitored in the environment, but that can induce undesirable effects in living beings [2,3].

The establishment of simultaneous analytical procedures for EOCs have been strongly encouraged due their practical applications [1,4,5]. Many sensitive procedures were already reported using chromatographic [4–6] and spectroscopic methods [4,6], but the use of large amounts of organic/toxic solvents, complex pretreatments of the samples, cost and long analysis time had limited their application on routine analysis [4,6,7]. Electroanalytical methods overcome the above-mentioned limitations, besides offer suitable sensitivity and selectivity; robust methods; operational simplicity; possibility of miniaturization; *in situ* analysis, and consequently better cost-effective compared to other conventional methods used in environmental studies. However, simultaneous electroanalytical procedures for EOCs are still scarce and include only a small number of these compounds [6,7].

Numerous electrochemical sensors were proposed for simultaneous screening of target harmful compounds (personal care products, licit and illicit drugs, phenols, dyes, polycyclic aromatic hydrocarbons, pesticides, amongst others recalcitrant pollutants) in environment matrices, generally based on their oxidation processes [7,8]. Nevertheless, for some chemicals (*i.e.*, compounds containing the groups –C=O, HO–C=O, $^{-}$O–C=O, –S=O, –N=N–, N–N=O, and other closely related structures), the reduction processes can be more suitable since the commonly metabolites found in the samples are not electroactives in usual potential window, reducing interferences on electroanalysis [9,10]. Unfortunately, very few electrodes have an appropriate potential window for this purpose, hampering the development of more efficient electroanalytical methods, denoting the necessity of research in this issue.

Mercury (Hg)-based electrodes are still among the most sensitive sensors to evaluate the electroreduction of organic molecules [9–11]. They display a wide cathodic potential range due to its high hydrogen overvoltage, permitting the reduction of several compounds. With the rise of Green Chemistry, the cost-benefit of these devices came to be questioned, but it is important to highlight that Hg is practically innocuous at room temperature, i.e., the formation of toxic by-products is remote, reinforcing its applicability for electrochemical studies. In addition, the miniaturization and automation of these sensors, with emphasis on hanging mercury drop electrode – HMDE (a fine glass capillary containing a static and renewable mercury drop at the end of the tube), the amount of mercury used for one scanning was dramatically decreased [9,10]. The toxicity of Hg-residues can be further neglected using efficient technologies to store them in a safe way (amalgamation, vitrification, thermal treatments, encapsulation, and stabilization/solidification processes), until their suitable treatment [12].

Prior studies carried out by our group with EOCs, it was assessed the possibility to determine different harmful pollutants to the environment on HMDE with high sensitivity, specificity and/or selectivity [13–15]. This report contemplates a simultaneous electrochemical method to determine tartrazine (TRT, azo-dye), dexamethasone (DMZ, steroidal anti-inflammatory) and diclofenac (DCL, non-steroidal anti-inflammatory) in raw and secondary effluent. TRT, DMZ and DCL (Fig. 1) are worldwide used by pharmaceutical industry in a variety of formulations. Together with their metabolites, they can strongly affect the ecosystems due to their toxicity and recalcitrant character, even at very low concentration, apart the supposed behavior as endocrine disruptor [13,16–18]. The simultaneous electrochemical sensing was performed on the HMDE allied to square-wave voltammetry (SWV), after sample concentration by solid-phase extraction method (SPE). Insights about the kinetic properties, electroreduction mechanism and the optimization of important electroanalytical parameters were also assessed.

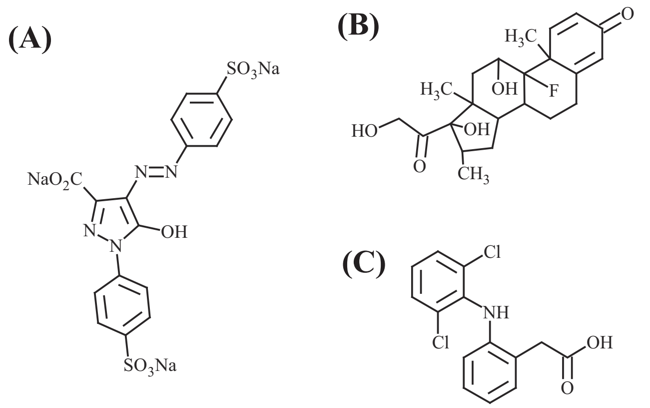

**Fig. 1.** Molecular structure of (A) tartrazine – TRT, (B) dexamethasone – DMZ, and (C) diclofenac – DCL.

## 2. Materials and methods

### 2.1. Chemicals

Analytical grade reagents, without further purification, were employed in all experiments. TRT (CAS: 1934-21-0), DMZ (CAS: 50-02-2) and DCL (CAS: 15307-79-6) were purchased from Sigma–Aldrich, Brazil. The acids and their conjugate bases used to prepare McIlvaine, Britton–Robinson, citrate, acetate e perchlorate buffers (pH 2.5), tested as supporting electrolytes, were supplied by Vetec, Brazil. Standard solutions were prepared from $1.0 \times 10^{-3}$ mol L$^{-1}$ TRT, DMZ and DCL aqueous stock solutions, and diluted with ultrapure water ($\rho = 18$ M$\Omega$ cm$^{-1}$) until the desired concentration. When necessary, the pH of the solutions was adjusted by adding appropriate amounts of 1.0 mol L$^{-1}$ NaOH.

### 2.2. Apparatus

The voltammetric experiments were carried out with a potentiostat/galvanostat Autolab PGSTAT 30 (Metrohm-Eco Chemie) and controlled by GPES 4.9 software. A conventional electrochemical cell with a three-electrode system was used, consisting of a HMDE (663 VA Stand, Metrohm-Eco Chemie) with surface area of 0.52 mm$^2$ as working electrode, a graphite rod as auxiliary electrode, and $Ag_{(s)}/AgCl_{(s)}/Cl^{-}_{(aq)}$ (saturated KCl) as reference electrode. The extraction of analytes from the wastewaters was made by SPE [1], using DSC-18 cartridges (500 mg/6 mL, Supelco) coupled to a Vacuum Manifold system (Supelco). A Micronal® B474 pH meter equipped with a glass combined electrode was used to adjust the pH values. All the solutions were prepared in ultrapure water from a Milli-Q system (Millipore Corp.).

### 2.3. Wastewater sampling

Wastewater samples were collected from two full-scale wastewater treatment plants, namely Tabapuá (Tab-TP) and Conjunto José Walter (CJW-TP), located in the state of Ceará, a semi-arid zone in Brazil. Both studied treatment plants receive and treat a combination of domestic and industrial wastewaters. The treatment technology employed was waste stabilization pond, consisting of one facultative followed by two maturation ponds in series. The influent and effluent samples were analyzed in order to assess