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
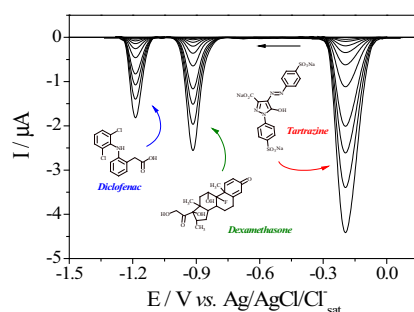
ABSTRACT

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 2.78×10^{-8} to 1.48×10^{-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.

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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

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
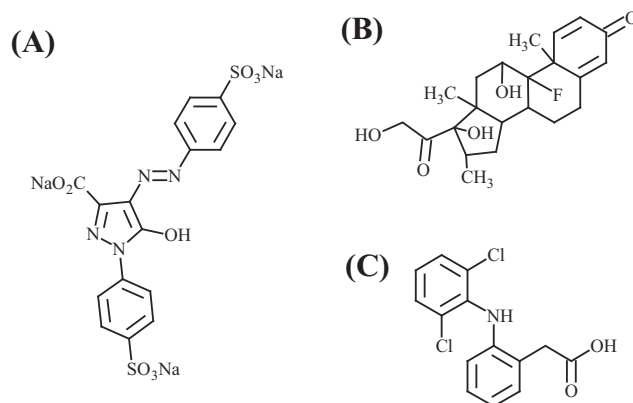

Fig. 1. Molecular structure of (A) tartrazine – TRT, (B) dexamethasone – DMZ, and (C) diclofenac – DCL.

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.

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 1.0×10^{-3} mol L^{-1} TRT, DMZ and DCL aqueous stock solutions, and diluted with ultrapure water ($\rho = 18$ MΩ 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

the efficiency of the employed treatment technology for the removal of the investigated EOCs. The wastewater samples were collected with amber glass flasks, preserved with methanol (5 mL L^{-1}) and kept at 4 °C until the SPE procedure. The assays were performed up to 48 h after sampling.

2.4. Solid-phase extraction of the analytes

The wastewater samples were initially filtered in 0.45 μm glass-fiber under vacuum, and then the pH was adjusted to 3.0 by addition of 50% (v/v) HCl. The samples, typically 500 mL, were then loaded onto the cartridges (preconditioned with 10 mL of hexane, acetone, methanol, and ultrapure water) at a flow rate of 8 mL min^{-1}. Posteriorly, the cartridges were dried for 30 min under vacuum and eluted with 4 mL of acetone:hexane (50:50, v/v) solution. Extracts collected in amber glass flasks were dried in an oven at 45 °C, for a period of 8 h. Finally, the resultant material was redissolved in 10 mL of citrate buffer (pH 2.5) and further analyzed by the proposed electrochemical procedure.

2.5. Electroanalytical procedure

Initially, the electroactivity of TRT, DMZ and DCL on HMDE was investigated by SWV from 0.0 V to −1.4 V, using different electrolytes (pH 2.5). Before each experiment, the medium was stirred with a stream of high-purity N$_2$ (White Martins Praxair Inc., Brazil) bubbled in the solution for 2 min. Then, we selected the best electrolyte and pH for the electroanalysis, based on maximum value of the faradaic current obtained for each redox process. Cyclic voltammetry (CV) technique was also used to study the adsorptive character of the chemicals, kinetic and mechanistic parameters, and the influence of the scan rate (v) on selectivity and sensitivity of the proposed procedure.

The single and simultaneous quantifications of the compounds were performed by SWV following a systematic study of the pulse potential frequency (f), amplitude of the pulse (a) and height of the potential step (ΔE_s), which are experimental parameters that affect the responses in this technique. The optimization of these variables was based on the intensity of the peak currents (I_p), displacement of the peak potentials (E_p), alteration of the half-peak width ($\Delta E_{p/2}$) and noise/signal ratio.

Thereafter, analytical curves were obtained in supporting electrolyte from the correlation between I_p and the concentration of the analytes. The detection (LOD) and quantification limits (LOQ) were estimated by the quotient between the standard deviation of the intercepts and the average of the slopes, obtained from the linear regression equations of analytical curves, according the IUPAC recommendation [19]. Repeatability and precision of the proposed electroanalytical procedure were assessed by the relative standard deviations (RSD) of ten determinations performed on the same day (intra-day) and on different days (inter-day) using the same solution.

The proposed procedure was used to quantify TRT, DMZ and DCL in influents and effluents from full-scale sewage treatment plants, after samples concentration by SPE method. When one of these compounds was not found directly in the samples, a spiking was made to investigate the applicability and accuracy of the method. All experiments were taken at 25 °C and the results were presented as the average of three measurements.

3. Results and discussion

3.1. Electroactivity and redox behavior of the chemicals

The target compounds have carboxylic group derivatives and aromatic rings distributed in their structures, and this fact increases the possibility of interaction and/or overlap of their redox processes. Thus, we performed single and simultaneous electroactivity tests of TRT (1.31 × 10^{-5} mol L^{-1}), DMZ (2.59 × 10^{-5} mol L^{-1}) and DCL (4.59 × 10^{-5} mol L^{-1}) on HMDE, using SWV (f = 100 s^{-1}, a = 50 mV and ΔE_s = 2 mV) technique, from 0.0 to −1.4 V. Moreover, considering the proton-dependent character of these chemicals [13,16,18], McIlvaine, Britton-Robinson, citrate, acetate and perchlorate buffer solutions (pH 2.5) were used, so that H$^+$ concentration was kept constant. The results showed distinct and well-defined cathodic peaks for TRT, DMZ and DCL in all electrolytes, both in single and simultaneous way, evidencing the possibility of simultaneous determination, since the response obtained for each compound was not affected in the presence of others. The reduction processes with more intense I_p, less negative E_p and more separated peaks, especially for DMZ and DCL, were registered in citrate buffer (Fig. 1S – Supplementary Material), justifying its choice as electrolyte for the subsequent experiments.

A representative simultaneous square-wave voltammogram for TRT (0.22 V), DMZ (0.93 V) and DCL (1.12 V), obtained on HMDE and in citrate buffer (pH 2.5), is presented at Fig. 2. Analyzing the current components, it was observed that the resultant and forward components were in the same direction, while the backward component was null for TRT and DMZ, while for DCL it went in opposite direction and with lower intensity than the other current components. From these informations and employing the other diagnostic criteria of this technique [20,21], the reduction processes of TRT and DMZ were classified as irreversible, and DCL as quasi-reversible, corroborating previously reported data [13,16,18].

Tests were also performed with other Hg-based electrodes (bare polished silver solid amalgam electrode, with Ag/Hg (30:70%, m/m); and modified with Hg-meniscus), but problems relative to low reproducibility and sensitivity, besides lower potential window compared to HMDE, limited their applications.

3.2. Effect of the pH and mechanistic insights

Considering the proton-dependence of the chemicals, the influence of the pH (2.5–6.5) was also evaluated by SWV, obeying the buffer capacity of the electrolyte. The increase of the pH provided a decrease of I_p values for all compounds. We also observed a parallel displacement of E_p toward more negative values for TRT and DMZ, but on opposite direction for DCL. These observations are related with the equilibrium of protonated/deprotonated species in solution and the acid dissociation constants (pK_a) of TRT, DMZ and DCL.
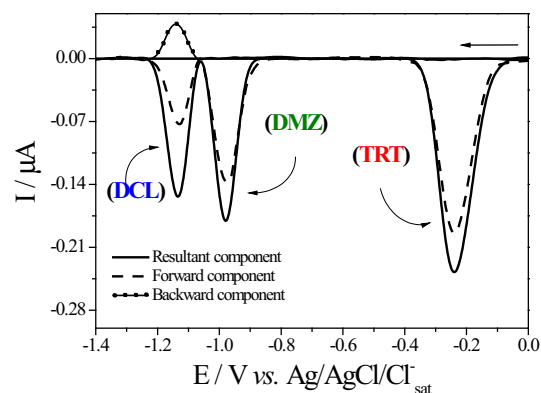

Fig. 2. Simultaneous square-wave voltammogram obtained for TRT (1.31 × 10^{-5} mol L^{-1}), DMZ (2.59 × 10^{-5} mol L^{-1}) and DCL (4.59 × 10^{-5} mol L^{-1}) on HMDE, with its respective current components, using citrate buffer pH 2.5 as electrolyte, and employing f = 100 s^{-1}, a = 50 mV and ΔE_s = 2 mV.

According to Gómez et al. [16], TRT have three acid dissociation constants related to protonation of two sulfonic acids (pK_{a1} = 2.0), an acetate (pK_{a2} = 5.0), and an azo (pK_{a3} = 10.8) group. Medeiros et al. [22] studied the electroreduction mechanism of synthetic dyes and concluded that azo-dyes are reduced through one electrochemical process involving $4e^-$ and $4H^+$, generating secondary amines as final product. In case of DMZ, Oliveira et al. [13] showed that this steroid suffer two protonation, related to unconjugated (pK_{a1} = 1.9) and conjugated (pK_{a2} = 6.4) ketone groups, respectively. These same authors also complemented that the electroreduction of each ketone group involves $2e^-$ and $2H^+$ (i.e., $4e^-$ and $4H^+$ per reduced molecule), producing a vicinal diol linked to sp^2-carbons as final product, called pinacole. As for the DFN, Mokhtari et al. [18] affirmed that it has a single acid ionization constant (pK_{a1} = 4.0) related to protonation of the amine group linked to the aromatic rings, which constitutes the mainly nucleophilic center of this molecule. For these authors, the reduction of DCL is represented by one electrochemical process involving $2e^-$ and $2H^+$, where the carboxylic group is reduced to germinal diol. The Fig. 3 illustrates the general reaction involved in electrochemical reduction of EOCs under study.

Still concerning the pH, we evidenced the overlapping of DMZ and DCL peaks from pH 3.5, make it virtually indistinguishable at

pH $\geqslant$ 4.5, where just one voltammetric signal with low intensity was registered. Thus, considering that the focus of this work is the simultaneous determination of TRT, DMZ and DFN, it was selected pH 2.5 as optimized condition.

3.3. Effect of the scan rate and evaluation of kinetic parameters

The influence of the scan rate on the peak potential separation was evaluated by CV (100–900 mV s^{-1}) in citrate buffer pH 2.5, containing 1.31×10^{-5} mol L^{-1} TRT, 2.59×10^{-5} mol L^{-1} DMZ and 4.59×10^{-5} mol L^{-1} DFN. As can be seen at Fig. 4, three well-defined cathodic peaks were recorded, and just one anodic peak with low intensity for all scan rates was observed. Comparing these data to those obtained with each compound singly, it is affirmed that the peaks 1 and 2 are related to irreversible redox processes of TRT and DMZ, respectively, while the peaks 3 and 4 correspond to quasi-reversible process of DFN, corroborating the preliminary remarks obtained by SWV and prior scientific reports [13,16,18]. Thus, the overpotential order found for the reduction of the compounds on HMDE was TRT < DMZ < DFN.

For all compounds, the increase of v provided the displacement of E_p to more negative values, besides better separation between the reduction processes of the EOCs under study, indicating that
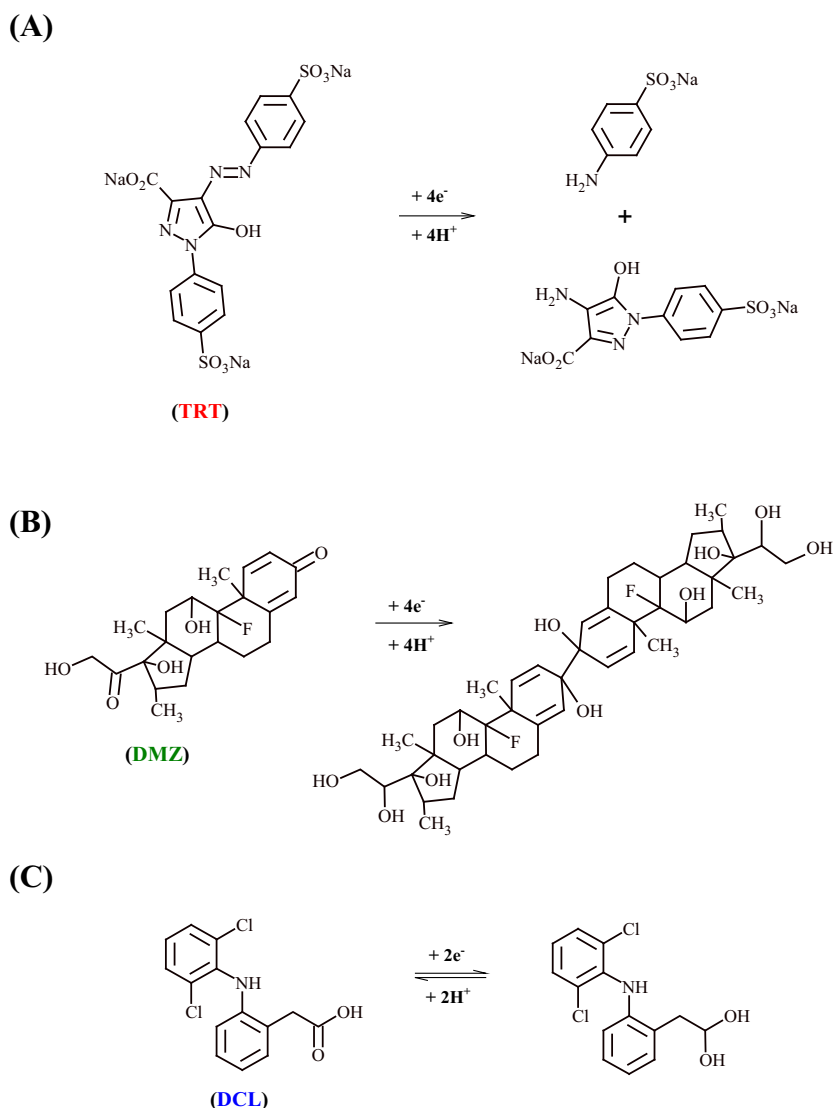
(A)

(B)

(C)

Fig. 3. General electrochemical reaction for the reduction of (A) TRT, (B) DMZ, and (C) DCL on the HMDE, using citrate buffer pH 2.5 as electrolyte.
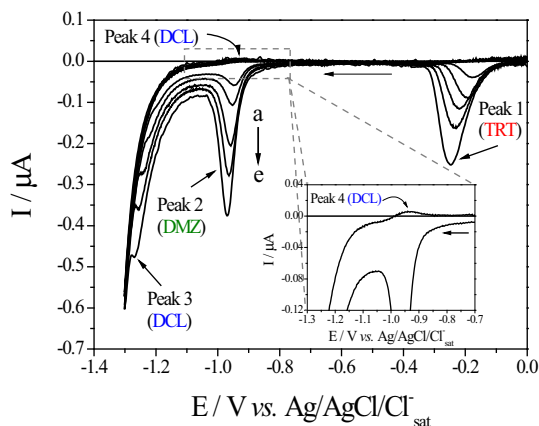
Fig. 4. Simultaneous cyclic voltammograms obtained for TRT (1.31×10^{-5} mol L^{-1}), DMZ (2.59×10^{-5} mol L^{-1}) and DCL (4.59×10^{-5} mol L^{-1}) on HMDE, using citrate buffer pH 2.5 as electrolyte, with scan rates of (a) 100, (b) 300, (c) 500, (d) 700, and (e) 900 mV s^{-1}. The insert refer to amplification of the anodic process of DCL at 100 mV s^{-1}.

more elevated v values aid on selectivity of the proposed procedure. It was also observed a linear increase between I_p and v values, showing that the charge-transfer processes of the compounds on HMDE were controlled by adsorption [20]. The found linear regression equations are described below:

$$I_{p(TRT)}/\mu A = -7.00 \times 10^{-3} - 2.71\,v/mV\,s^{-1}(r = 0.9993) \quad (1)$$

$$I_{p(DMZ)}/\mu A = -1.23 \times 10^{-2} - 4.00\,v/mV\,s^{-1}(r = 0.9986) \quad (2)$$

$$I_{p(DFN)}/\mu A = -7.46 \times 10^{-3} - 5.54\,v/mV\,s^{-1}(r = 0.9909) \quad (3)$$

The adsorptive character of TRT, DMZ and DCL was also confirmed through the consecutive potential scans, where a pronounced decrease of I_p values was identified from the second scan, becoming null on posterior cycles, due to block of the HMDE active area.

In addition, the CV experiments also showed that DCL redox pair was only registered from $v \geqslant 100$ mV s^{-1} (insert of Fig. 4), suggesting fast electrodic kinetics on the working electrode. Despite the probable differences of reaction orders, the DCL electrodic kinetics was probably higher than other compounds, since TRT and DMZ redox process were already detected from $v \geqslant 10$ mV s^{-1}.

Knowing the reversibility of the compounds and using SWV frequency data, it was possible to determine some theoretical kinetic parameters [21]. In case of irreversible processes of the TRT and DMZ, the electronic transference coefficient (α) can be calculated by the following equation:

$$\frac{\partial E_p}{\partial \log f} = \frac{-2.3RT}{\alpha nF} \quad (4)$$

where n represents the number of transferred electrons, F is the Faraday constant, and the other variables have their usual significance. Substituting the terms, we found $\alpha_{(TRT)} = 0.91$ and $\alpha_{(DMZ)} = 0.83$. From the relationship between I_p and f, it was also possible to estimate the theoretical kinetic constant (k_s) of the TRT and DMZ electrochemical processes. Using the Eq. (5), we obtained $k_{s(TRT)} = 1.90 \times 10^{-9}$ A s and $k_{s(DMZ)} = 1.45 \times 10^{-9}$ A s. In summary, the kinetics of electron-transfer for TRT and DMZ on HMDE were very similar, since the α and k_s values were only slightly different:

$$k_s = Ip/f \quad (5)$$

Regarding the DFN, from the relationship between I_p/f versus f, a maximum frequency (f_{max}) of 150 s^{-1} was obtained. Substituting this value in Eq. (6), it was estimated the k_s of the electrochemical process, considering κ_{max} a critic kinetic parameter:

$$k_s = \kappa_{max} \cdot f_{max} \quad (6)$$

For quasi-reversible systems, when α is not exactly known ($0.25 \leqslant \alpha \leqslant 0.85$), κ_{max} can be considered 1.18 ± 0.05. Making this consideration, we found $k_{s(DFN)} = 177$ s^{-1}, suggesting a fast electrodic kinetics of this molecule on the HMDE. This data set also justifies the register of the DCL reduction process only for $v \geqslant 100$ mV s^{-1}.

3.4. Optimization of the square-wave voltammetry parameters

In order to obtain better analytical sensitivity for the quantification of TRT, DMZ and DCL residues, the square-wave voltammetry parameters, i.e., f (10–700 s^{-1}), a (5–60 mV) and ΔE_s (1–7 mV), were evaluated and $f = 150$ s^{-1}, $a = 30$ mV and $\Delta E_s = 3$ mV were selected due to higher I_p, less negative E_p, smaller $\Delta E_{p/2}$ and better noise/signal relation.

Knowing about the strong adsorptive character of TRT, DMZ and DCL on the HMDE, the influence of the accumulation potential (0–1.4 V) and time (5–60 s) were also inquired, but the sensitivity of the proposed procedure was not improved for the three compounds simultaneously and thus, these parameters were not used to construct the analytical curves.

3.5. Analytical curves

From the reduction processes of TRT (0.22 V), DMZ (0.93 V) and DCL (1.12 V) on the HMDE, obtained in citrate buffer pH 2.5, and
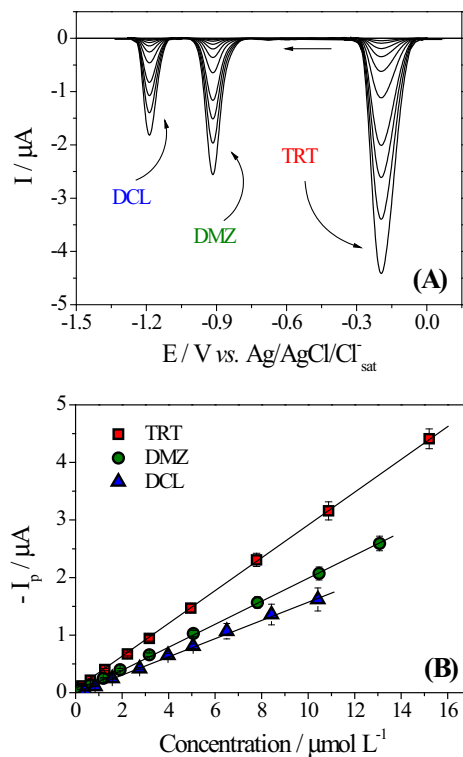

Fig. 5. (A) Simultaneous square-wave voltammogram obtained for TRT (2.00×10^{-8} to 1.52×10^{-5} mol L^{-1}), DMZ (2.13×10^{-7} to 1.32×10^{-5} mol L^{-1}) and DCL (4.00×10^{-7} to 9.11×10^{-6} mol L^{-1}) on HMDE, using citrate buffer pH 2.5 as electrolyte, and employing $f = 150$ s^{-1}, $a = 30$ mV and $\Delta E_s = 3$ mV. (B) Analytical curves constructed from the prior voltammograms, with the respective error bars for each concentration studied.

using the optimized SWV conditions ($f = 150 \text{ s}^{-1}$, $a = 30$ mV and $\Delta E_s = 3$ mV), the analytical curves were constructed for the single (Fig. 2S – Supplementary Material) and simultaneous determination of these compounds. The results showed that the linear concentration ranges and sensitivity, in terms of LOD and LOQ, were relatively better for the single determination. The order of sensitivity achieved for the single determination was TRT (LOD = 9.90×10^{-9} mol L^{-1} and LQ = 4.28×10^{-8} mol L^{-1}) > DMZ (LOD = 3.21×10^{-8} mol L^{-1} and LOQ = 7.83×10^{-8} mol L^{-1}) > DCL (LD = 9.90×10^{-8} mol L^{-1} and LQ = 2.56×10^{-7} mol L^{-1}). However, the single electroanalytical determination were disadvantageous if compared to simultaneous, due to the higher cost, longer period for the analyses and the large amount of generated residues.

Simultaneous electroanalytical sensing (Fig. 5A) was able to detect trace concentrations of TRT (LOD = 2.78×10^{-8} mol L^{-1} and LOQ = 9.28×10^{-8} mol L^{-1}), DMZ (LOD = 4.23×10^{-8} mol L^{-1} and LOQ = 1.41×10^{-7} mol L^{-1}) and DCL (LOD = 1.48×10^{-7} mol L^{-1} and LOQ = 4.94×10^{-7} mol L^{-1}), with high repeatability (relatively standard deviation of the intra-day and inter-day measurements below 5.0%) and low dispersion of the analytical data (r ranging from 0.9986 to 0.9992). The high precision of the measurements can be also observed by the short error bars presented at the Fig. 5B. A summary of the analytic performance achieved is described at Table 1.

It is noteworthy that sensitivity obtained in this work was similar or even higher than those published by other authors on electroanalytical studies with these compounds (Table 2). In other words, using the HMDE as working electrode, a single potential

scan on a millimetric Hg-drop was enough to simultaneously determine trace concentrations of the EOCs under study, through a simple, selective, quick and relatively cheap electroanalytical protocol. These advantages make this procedure a promising alternative for the simultaneous monitoring of TRT, DMZ and DCL in complex samples, such as influents and effluents from full-scale sewage treatment plants.

3.6. Application in wastewater samples

The proposed procedure was used to determine TRT, DMZ and DCL in wastewater from the stations of Tab-TP and CJW-TP, presented at the Section 2.3., in order to evaluate the accuracy of the simultaneous electroanalytical method. The analyses were performed in samples collected before (Tab-TP-1 and CJW-TP-1) and after (Tab-TP-2 and CJW-TP-2) the conventional treatment employed at these stations. The physicochemical characterization of these samples (Table 1S – Supplementary Material) revealed high levels of organic matter and nutrients, which increase the complexity of the samples for analytical purposes and limit the application of many analytical procedures available. Thus, was made a prior extraction of the analytes by the SPE method, with the intention to remove the excess of organic matter and humic substances in the matrices, which adsorb on the HMDE and block its electroactive area.

Through the standard addition method, we found TRT and DCL directly in all samples. Representative square-wave voltammograms obtained for the studied wastewaters can be seen at Fig. 6. The concentrations of TRT ranged from 1.06×10^{-8} mol L^{-1} to 6.82×10^{-8} mol L^{-1}, while the DCL levels ranged from 3.27×10^{-8} mol L^{-1} to 1.03×10^{-7} mol L^{-1}. The highest concentrations were detected in samples collected before the employed wastewater treatment (TRT = 1.13×10^{-8} mol L^{-1} and DCL = 4.74×10^{-8} mol L^{-1} for Tab-TP-1; TRT = 6.82×10^{-8} and DCL = 1.03×10^{-7} for CJW-TP-1), although these values are close to those obtained after this process. These results prove that stabilization and maturation pond type technology were not suitable to completely remove these contaminants, therefore being necessary a complementary treatment process.

Since the DMZ was not found directly in the samples, we did the spiking (9.90×10^{-7} mol L^{-1}) to evaluate the efficiency and accuracy of the electroanalytical proposed procedure. The recuperation values ranged from 97.8% ± 0.2 (before the treatment) to 98.6% ± 0.4 (after the treatment), reinforcing the success of this proposal. The high precision of the assays was confirmed through the relative standard deviation of the measurements (below

Table 1
Figure of merit for the simultaneous analysis of TRT, DMZ and DCL, achieved under optimized conditions.

Parameter	Emerging organic contaminants		
	TRT	DMZ	DCL
Linear range (mol L^{-1})	2.00×10^{-8} to 1.52×10^{-5}	2.13×10^{-7} to 1.32×10^{-5}	4.00×10^{-7} to 9.11×10^{-6}
Intercept (A)	1.71×10^{-6}	1.12×10^{-6}	-1.76×10^{-7}
±Confidence interval	$\pm 7.62 \times 10^{-9}$	$\pm 4.99 \times 10^{-9}$	$\pm 7.84 \times 10^{-9}$
Slope (A mol^{-1} L)	7.80	2.16	2.07
±Confidence interval	$\pm 3.48 \times 10^{-2}$	$\pm 9.62 \times 10^{-3}$	$\pm 9.22 \times 10^{-3}$
r	0.9991	0.9992	0.9986
LOD (mol L^{-1})	2.78×10^{-8}	4.23×10^{-8}	1.48×10^{-7}
LOQ (mol L^{-1})	9.28×10^{-8}	1.41×10^{-7}	4.94×10^{-7}
Intra-day repeatability (%RSD)	2.51 ± 0.05	2.63 ± 0.03	3.78 ± 0.08
Inter-day repeatability (%RSD)	4.05 ± 0.10	4.55 ± 0.09	4.83 ± 0.12

Table 2
Comparison of the detection limits achieved for TRT, DMZ and DCL by the present proposes and others developed with different sensors.

| Target compound	Working electrode	Detection limit	References
TRT	β-Cyclodextrin-coated poly (diallyldimethylammonium chloride)-functionalized graphene composite film modified glassy carbon-rotating disk electrode	1.25×10^{-8} mol L^{-1}	[23]
	Graphene layer-wrapped phosphotungstic acid hybrid-modified glassy carbon electrode	30 µg L^{-1}	[24]
	Cathodically pretreated boron-doped diamond electrode	6.27×10^{-8} mol L^{-1}	[22]
	HMDE	2.78×10^{-8} mol L^{-1} or 14.8 µg L^{-1}	This work
DMZ	Edge-plane pyrolytic graphite electrode modified with single-walled carbon nanotubes	9.10×10^{-10} mol L^{-1}	[25]
	Fullerene-C$_{60}$-modified pyrolytic graphite electrode	5.50×10^{-8} mol L^{-1}	[17]
	HMDE	2.00×10^{-7} mol L^{-1}	[26]
	HMDE	4.23×10^{-8} mol L^{-1}	This work
DCL	Carbon paste electrode modified with multiwall carbon nanotubes and 1-butyl-3-methylimidazolium hexafluoro phosphate as a binder	9.00×10^{-8} mol L^{-1}	[27]
	Cu-doped zeolite-expanded graphite-epoxy composite electrode	Until 3.00×10^{-7} mol L^{-1}	[28]
	Multi-walled carbon nanotubes-dihexadecyl hydrogen phosphate film-coated glassy carbon electrode	8.00×10^{-8} mol L^{-1}	[29]
	HMDE	9.90×10^{-8} mol L^{-1}	This work
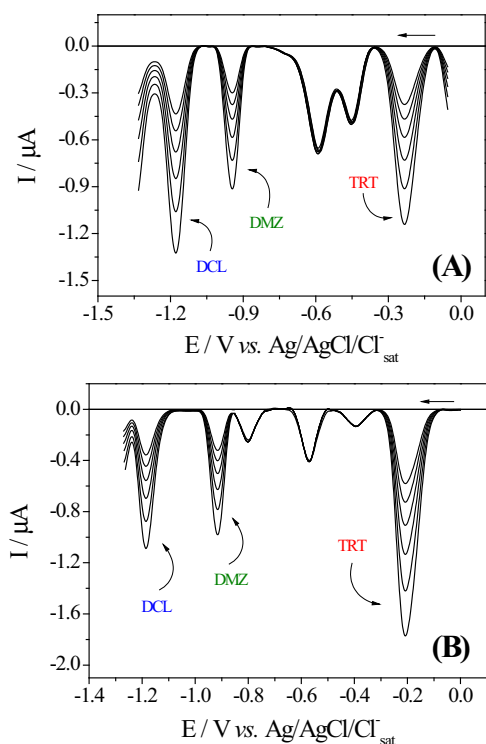
Fig. 6. Representative simultaneous square-wave voltammograms for the determination of TRT (6.35×10^{-7} to 7.78×10^{-6} mol L^{-1}), DMZ (1.18×10^{-6} to 1.05×10^{-5} mol L^{-1}) and DCL (1.57×10^{-6} to 8.42×10^{-6} mol L^{-1}) in wastewater from (A) Tab-TP-1 and (B) CJW-TP-1, through the standard addition method. Experimental conditions: HMDE working electrode; citrate buffer pH 2.5 as electrolyte; f = 150 s^{-1}; a = 30 mV and ΔE_s = 3 mV. The results for Tab-TP-2 and CJW-TP-2 were similar, with small alterations in intensity of the peak currents.

4.0%), despite the complexity of the samples. Importantly, parallel reduction processes of other contaminants were also identified in all samples. Whereas the redox sites of the studied chemicals are constituted by azo, ketone and carboxylic groups, any compound containing the same groups could affect the electrochemical response. However, the results showed that the other contaminants found did not affect the signal of the targeted compounds, with only small fluctuations on baselines.

In Brazil, unfortunately, there is no legislation that establishes a maximum value for the presence of TRT, DMZ and DCL in effluents so far, but this method has a set of analytical attributes that highlight it as an important alternative to monitor their residues in impacted environmental samples, such as wastewater from treatment plants.

4. Conclusions

A simultaneous electroanalytical method to determine TRT, DMZ and DCL at very low concentrations was developed, using SWV coupled to SPE method, and successfully applied to monitor these compounds in sewage treatment plants with high precision and accuracy. The selectivity of the sensing was strongly influenced by the electrodic kinetics of the compounds on HMDE, where a better separation between the redox peaks was obtained at more elevated scan rates. Employing the proposed simultaneous procedure, we found TRT and DCL directly in both raw and treated wastewater from Tab-TP and CJW-TP, indicating that the pond technology is unable to completely remove these contaminants, therefore requiring a post-treatment. The electroanalysis of the spiked samples showed the possibility to determine all compounds

with suitable selectivity, even in the presence of other electroactive contaminants. Finally, the proposed procedure can be an excellent alternative for monitoring TRT, DMZ and DCL in complex environmental samples such as sewage and other industrial wastewaters.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.01.003.

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