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Triclosan Detection in Aqueous Environmental Matrices by Thin-Films Sensors †

Cátia Costa Magro [1,*], Paulo Morgado Zagalo [2], João Pereira-da-Silva [2], Eduardo Pires Mateus [1], Alexandra Branco Ribeiro [1], Paulo António Ribeiro [2] and Maria Fátima Raposo [2]

[1] CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica 2829-516, Portugal

[2] CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica 2829-516, Portugal

* Correspondence: c.magro@campus.fct.unl.pt

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Abstract: Triclosan (TCS), a bacteriostatic detected in water bodies, have inauspicious effects in human and biota. Consequently, there is a critical need of monitoring these type of compounds in aqueous matrices. In this sense, sensors, based on polyethyleneimine and polysodium 4-styrenesulfonate layer-by-layer thin-films adsorbed on supports with gold interdigitated electrodes deposited, were developed. The aim was analyze the sensitivity of discrimination of TCS (10^{-15} M to 10^{-5} M) in deionized water, Luso® and in an effluent, by measuring the impedance spectra. LbL films can distinguish TCS concentrations in EF, while in LW was achieved an acceptable sensibility when interdigitated electrodes without films were used.

Keywords: triclosan monitoring; thin-films interdigitated sensors; impedance spectroscopy

1. Introduction

Water management is one of the most serious economic, political, social and ecological issues that mankind faces today. A major challenge is to keep water resources clean and safe, taking into account that the mixture of potential contaminants is continuously changing in a dynamic society. Over the last decade, beyond the legacy contaminants, (e.g., "priority" pollutants and industrial intermediates) that display persistence in the environment, new classes of environmental emerging organic contaminants, mainly composed of products used in a large scale in everyday life, are being detected and reported worldwide and accumulating in water, soil and biota [1]. Among them Pharmaceuticals and Personal Care Products, a group that includes numerous chemical classes, is under increased concern due to its continuous detection in water compartments and permanent introduction into environment across the world [2]. Triclosan (TCS) is a bacteriostatic used in household items such as toothpaste or soaps. TCS has raised health concerns that include allergy risk, antimicrobial resistance, developmental toxicity, and endocrine disruption [3–8]. The actual non-regulation demands the urgency of having reliable tools that will allow the real time monitoring of these emergent compounds [9–11].

The aim of the present work was explore the potential of electronic tongue concept [12,13] using thin-films sensors based on polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS)—to detect TCS spiked aqueous solutions: deionized water (DW), Luso® Portuguese mineral water (LW) and an effluent from a wastewater treatment plant (EF), with different concentrations (10^{-15} M to 10^{-5} M). The PEI/PSS thin-films with 5 bilayers $[PEI/PSS]_5$, with 10^{-2} M monomeric concentrations, were prepared by the layer-by-layer (LbL) technique onto solid supports with deposited gold electrodes sensors as described in [14]. The detection of TCS was achieved by measuring the

impedance spectra of thin-films when immersed in the TCS aqueous solutions. The impedance spectra were measured, using a Solartron 1260 Impedance Analyzer, in the frequency range of 1 Hz to 1 MHz applying an AC voltage of 25 mV.

2. Results

The impedance spectra of $[PEI/PSS]_5$ LbL films adsorbed on glass supports with interdigitated electrodes when immersed in TCS solutions prepared with different waters were measured. For comparison, the impedance spectra of glass support with interdigitated electrodes were also measured in the same conditions. Some examples of the obtained results are presented here. Figure 1a1,c1 show the resistance spectra of $[PEI/PSS]_5$ LbL film immersed in TCS solutions prepared with DW and EF, respectively. While Figure 1b1 shows the loss tangent spectra of interdigitated electrodes without LbL films immersed in TCS solutions prepared with LW. The dependence of electrical resistance and loss tangent as a function of the frequency for the $[PEI/PSS]_5$ combination was the better for DW and EF, contrary to LW where the best solution was the use of interdigitated electrodes without deposited thin-films. It seems that for more complex media, as LW or EF, the sensor is capable of discriminating TCS concentrations at high frequencies (LW [38,000 to 100,000 Hz]; EF [1000 to 10,000 Hz]), contrarily to DW [100 to 250 Hz]. From the measured spectra data, resistance and/or loss tangent at fixed frequencies were prepared. Figure 1a2,b2,c2 shows the resistance at 250 Hz, loss tangent at ~64 kHz and resistance at ~4 kHz plotted as a function of TCS concentration of the solutions prepared with DW, LW and EF, respectively. In the case of Figure 1a2, there is no clear tendency behavior, only a slight increment on the resistance between 10^{-15} M to 10^{-13} M, but still poor sensibility for the target molecule. Moreover, to LW the loss tangent tends to decrease with the increase of the TCS concentration, opposite to EF that increase the resistance with the increase of the TCS concentrations.

The adsorption of TCS onto polyelectrolytes thin-films, is affected by the pH of TCS solution [15]. The pH affected both the degree of ionization of the last polyelectrolyte in the LbL thin-film and the dissociation of TCS [16]. DW, LW and EF pH: 8.00, 5.80, 8.26. The acidic pH in in the LW, contributed to the slight desorption of the film. The desorption results, not shown here, were obtained measuring the ultraviolet-visible spectra of the films before and after immersion in the TCS solutions in an UV-VIS 2101 PC Scanning spectrophotometer. Hence, as previous observed, the best sensor to this water was gold interdigitated electrodes without deposited thin-films. Also, in more complex media, as EF matrix, [higher conductivity] the high amount of molecules promotes a higher fixed of the thin-films into the solid supports, having therefore less propensity to desorption or adsorption phenomena.

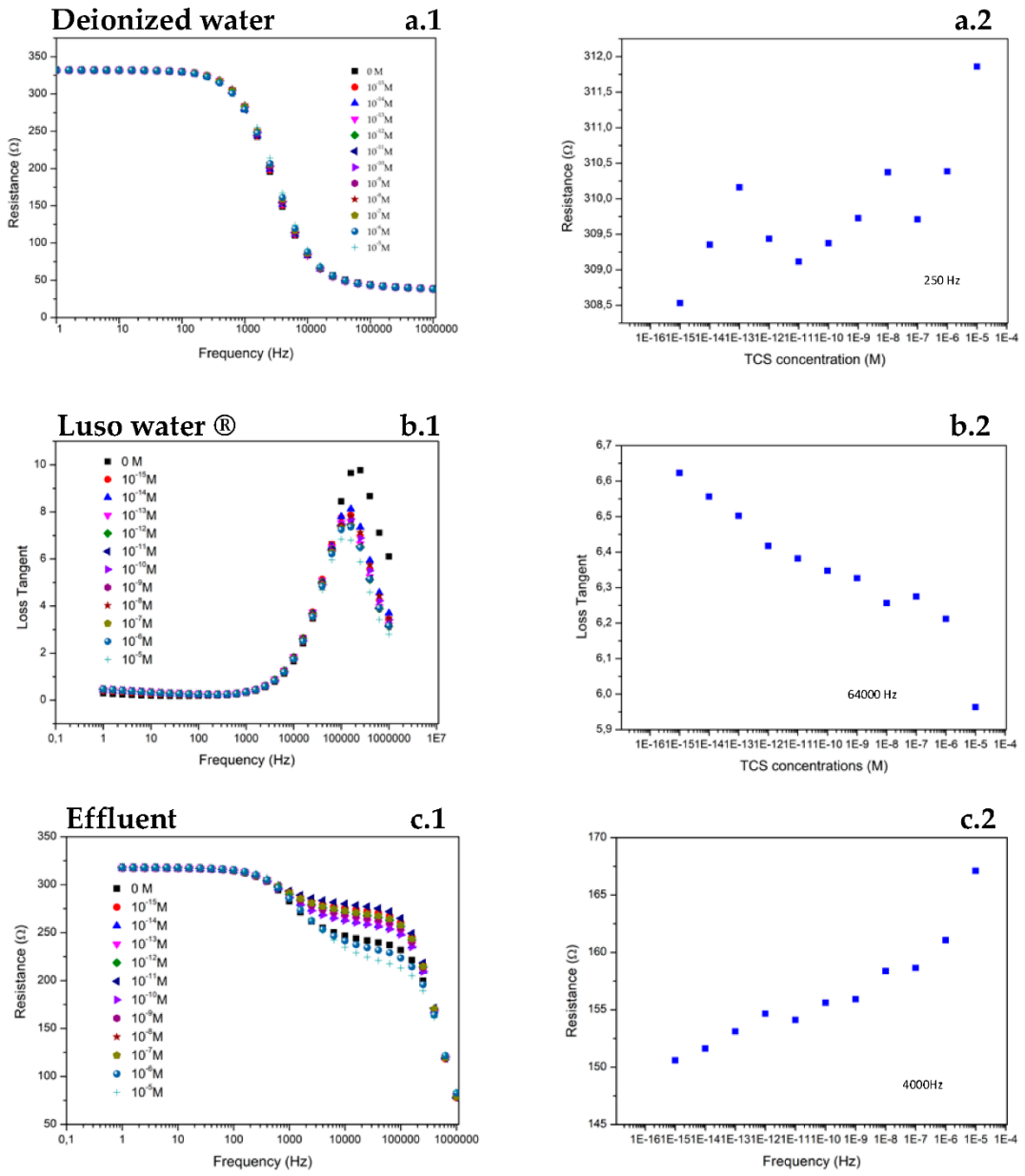

Figure 1. (**a1**) Resistance spectra of $[PEI/PSS]_5$ LbL film immersed in TCS solutions prepared with DW and (**a2**) Resistance at 250 Hz vs. TCS solutions prepared with DW; (**b1**) loss tangent spectra of interdigitated electrodes without LbL films immersed in TCS solutions prepared with LW and (**b2**) Loss tangent at 64 kHz vs. TCS solutions prepared with LW; (**c1**) Resistance spectra of $[PEI/PSS]_5$ LbL film immersed in TCS solutions prepared with EF and (**c2**) Resistance at 4000 Hz vs. TCS solutions prepared with EF.

3. Conclusions

The detection of TCS through impedance spectroscopy yielded acceptable results for $[PEI/PSS]_5$ in EF and interdigitated sensor with films in LW. To EF there was not observed desorption of the molecules of the films neither adsorption of TCS, confirming the sensor capability to detected TCS target molecule.

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writing—review and editing, C.C.M.; visualization, C.C.M.; supervision, E.P.M., A.B.R. and M.F.R.; project administration, A.B.R. and M.F.R.; funding acquisition, E.P.M., A.B.R., P.A.R. and M.F.R.

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