chemistry proceedings

MDPI

Proceedings

An Electronic Nose in Conjunction with An Electrochemical Molecularly Imprinted Polymer Sensor for Triclosan Sensing in Wastewater Samples †

Soukaina Motia [1,2], Benachir Bouchikhi [2], Nezha El Bari [1,*]

[1] Biosensors and Nanotechnology Group, Department of Biology, Faculty of Sciences, Moulay Ismaïl University of Meknes, B.P. 11201, Zitoune, Meknes, Morocco
[2] Sensor Electronic & Instrumentation Group, Department of Physics, Faculty of Sciences, Moulay Ismaïl University of Meknes, B.P. 11201, Zitoune, Meknes, Morocco
* Correspondence: n_elbari@hotmail.com

† Presented at the 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry, 01—15 July 2021; Available online: https://csac2021.sciforum.net/.

Abstract: In this study, a MIP sensor was developed for quantitative triclosan detection in wastewater samples. Qualitative analysis of the samples was also performed by using an electronic nose. The MIP sensor exhibits responses proportional to triclosan concentrations (0.1–1000 pg/mL) with a detection limit of 0.23 pg/mL. The sensor was applied for Triclosan detection in spiked wastewater samples with a significant recovery (99%). Radar plots constructed from E-nose responses show different chemical signatures according to analyzed samples. Results from both sensing systems were employed to build a model by using partial least scare (PLS) with correlation coefficient R = 0.98.

Keywords: Wastewater; electronic nose; multivariate data analysis; electrochemical sensor; triclosan.

Published: 01 July 2021

1. Introduction

Sewage systems are the key collection location for cosmetic residues, so their presence is unavoidable [1]. Triclosan (TCS) is identified as an antimicrobial agent against bacteria [2]. It has been broadly employed in personal care products, among other toothpastes. As a result of its extensive use and resulting transport, TCS is pervasive in the environment and is partly processed in a sewage treatment plants [3]. For the stated and mentioned reasons, it is very relevant to develop a simple, sensitive, and convenient method for the detection of TCS to sustain surveys on its environmental destiny. So far, certain methods for the determination of TCS have been documented, namely liquid chromatography coupled with mass spectrometry [4], spectrophotometry [5], and electrochemistry [6], etc. Whilst these methods have the advantage of a high accuracy, the majority of them represent some disadvantages like the high cost of the equipment, long analysis times, low sensitivity, and the need for trained personnel.

On one hand, the use of electrochemical sensors has seen enormous progress [7]. In particular, molecularly imprinted polymer (MIP), as a biomimetic receptor, would achieve the intended high mechanical and chemical stability, selectivity, reusability, and ease of synthesis [8]. Thus, the development of a strongly selective electrochemical MIP sensor based on the above considerations would be very challenging for the determination of the TCS.

On the other hand, electronic nose (e-nose) technology has emerged as a very encouraging approach for environmental analysis [9]. This approach has turned out to be simple, fast, and very promising for reducing the time and costs of analysis.

In this work, a novel platform is proposed to improve electrochemical techniques by developing a MIP sensor for quantitative TCS determination in wastewater samples. A second part of this study is devoted to the use of an e-nose system for the qualitative analysis of these samples spiked with TCS. Multivariate analysis methods based on partial least squares regression (PLS-R)) model was also used for a clearer interpretation and for the prediction of the TCS concentration in the studied samples.

2. Experimental

2.1. Reagents and Solutions

TCS, N-hydroxysuccinimide (NHS), carboxylic polyvinyl chloride (PVC-COOH), potassium ferrocyanide ($[Fe(CN)_6]^{4-}$), 1,4-Dioxane (99.8%), potassium ferricyanide ($[Fe(CN)_6]^{3-}$), 2,4,6-trichlorophenol, catechol, and phosphate buffered saline (PBS) were ordered from Sigma Aldrich. Acrylamide (AAM), N-(3-dimethylaminopropyl)-N′ ethylcarbodiimide hydrochloride (EDC), N, N′-methylene-bisacrylamide (NNMBA), and N, N, N′, N′-Tetramethyl-ethylenediamine (TEMED) were purchased from Fluka. Ammonium persulphate (APS) was obtained from Scharlau chemise S.A. Methanol, (Hydroxymethyl) aminomethane (TRIS 0.5 M) and acetic acid were all from VWR Chemicals. From a standard stock solution of TCS (1 mg/mL in methanol), working solutions were obtained by a dilution of the previous solution with PBS (pH = 7.4) [10]. All working solutions of the established range between 0.1 and 1000 pg/mL were stored at 4 °C until analysis.

Domestic wastewater samples were collected from the Kasba district of Meknes (Morocco), in pre-cleaned amber glass vials (20 mL). The wastewater samples vials were filled and quickly transferred to the laboratory for storage at 4°C until analysis. The samples were used directly to avoid degradation and consequent changes in properties. A vortex apparatus was used to homogenize the sample before analysis.

2.2. Aparatus

A potentiostat (Palmsens^3) interfaced to a computer and operated by PS-Trace software was employed for all electrochemical characterizations. Hence, the screen-printed gold electrode (Au-SPE) were connected to the Palmsens^3 by means of a junction box. As transducer, the Au-SPE electrode was used, consisting of a gold working (0.19 cm^2) and counter electrode (0.54 cm^2) as well as silver reference electrode. The electrodes were purchased from Sigma Aldrich, Spain.

2.3. Synthesis of the MIP Sensors

For the elaboration of the MIP sensor, the working area of the bare Au-SPE was cleaned by washing with ethanol (99.95 %) and distilled water. The PVC-COOH was dissolved in 1,4-dioxane at 40°C. Thus, 30 μL of a PVC-COOH solution, at 8.8 mg/mL in 1,4-dioxane is dropped onto the working Au-SPE, and was incubated for 90 min at room temperature. Afterward, to activate the –COOH groups of the resulting Au-SPE/ PVC-COOH, 30 μL of aqueous solution containing 4 mg/mL of EDC and 1 mg/mL of NHS, was incubated for 90 min [11]. The EDC and NHS molecules, which did not react, were removed by rinsing thoroughly with distilled water. In following, 30 μL of the TCS standard solution (1 mg/mL in methanol) was deposited on the electrode for 3 h at 4°C in order to allow TCS molecules binding with activated –COOH groups of the PVC-COOH film [12]. Then, the unbounded templates were removed by rinsing with the PBS buffer (pH = 7.4). The Au-SPE/ PVC-COOH/TCS electrode was then incubated for 30 min in 30 μL of TRIS solution (pH = 9) to significantly block no specific sites. Afterward, the polymer solution was prepared by 11 mg/mL of AAM and 71 mg/mL of NNMBA in PBS. APS (13 mg/mL in PBS) as polymerization initiator was added to the mixture. Then, a TEMED solution (5 %) as a catalyst was also added to accelerate the polymerization. From the obtained solution, 30 μL was deposited and incubated onto the working electrode during 5 h at 4°C. Finally, the TCS imprinted sites were obtained after extracting the template from the polymer by using 30 µL of a solution containing a mixture of methanol and acetic acid (7:3, (v/v)) that was incubated onto the modified surface for 15 min.

2.4. Electrochemical Methods

In the present study, all steps of the modification of the Au-SPE were monitored by using various electrochemical techniques, namely cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical characterizations were conducted by using 0.01 M PBS solution (pH 7.2) containing 5 mM $[Fe(CN)_6]^{4-/3-}$ as a redox probe [13]. CV were registered over the potential range of −0.4 to 0.6 V at a scan rate of 30 mV/s. The DPV technique was used over a potential range of −0.2 to 0.3 V with a scan rate of 50 mV/s. All measurements were carried out at room temperature (25 °C).

2.5. E-nose Measurement Set-Up

An e-nose system was employed to qualitatively investigate the five wastewater samples spiked with different TCS concentrations (0.1, 1; 10, 100, and 1000 pg/mL). Before starting the measurements, a 20 mL sample of water was placed in a 50 mL Erlenmeyer flask and kept at a temperature of 32 ± 0.5°C. Then the effluent transfer takes place: the collected volatile compounds are transferred to the sensor matrix. Pure nitrogen gas with a flow rate of 60 mL/min is used as carrier gas from the headspace to the measuring cell. The operational system is composed of three parts: the sensor chamber, the sampling system, and the data acquisition system as depicted in Figure 1.

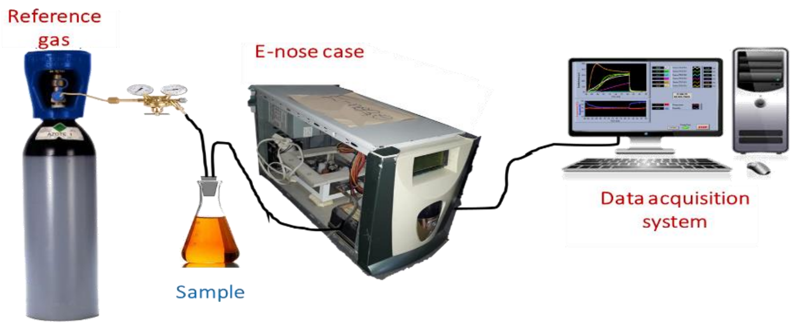

Figure 1. E-nose experimental setup used in these measurements [14].

This study is conducted using an e-nose based on the use of 6 TGS type gas sensors whose references and target gases are: TGS 815 (CH_4), TGS 821 (H_2), TGS 822 (Alcohols, Xylene and Toluene), TGS 824 (NH_3), TGS 825 (H_2S) and TGS 842 (methane)

3. Results and Discussion

3.1. Electrochemical Characterization of the MIP Assembly

Figure 2 illustrates cyclic voltammograms of the stepwise MIP sensor elaboration. After each immobilization, the current amplitude changes showing that the surface of the electrode is in the process of changing.

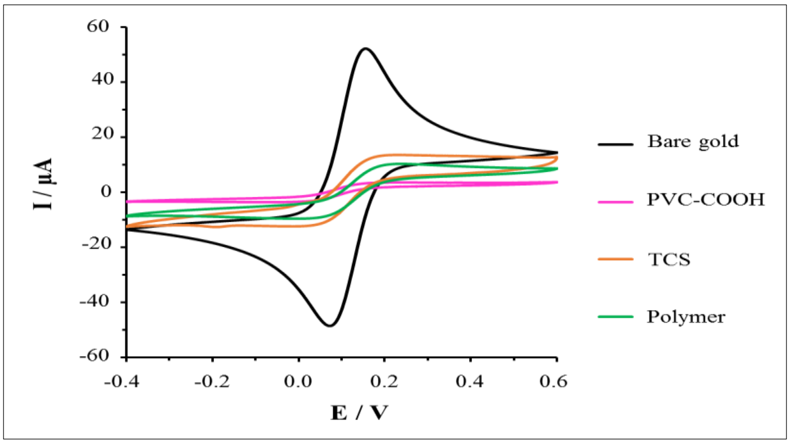

Figure 2. Cyclic voltammograms of the different stages of MIP sensor assembly.

3.2. MIP Sensor Responses

The corresponding obtained outcomes are depicted in Figure 3a. As TCS concentrations increased, the voltammograms current peaks become slower [15].

In the other side, the analytical curves between the recorded signals versus Logarithm of the TCS concentrations are represented in Figure 3b. For DPV method, a lower LOD was found to be 0.23 pg/mL. From these results and a comparison with the literature, we can conclude that the relevant MIP sensor exhibited a wider range (0.1-1000 pg/mL) and a lower detection limit.

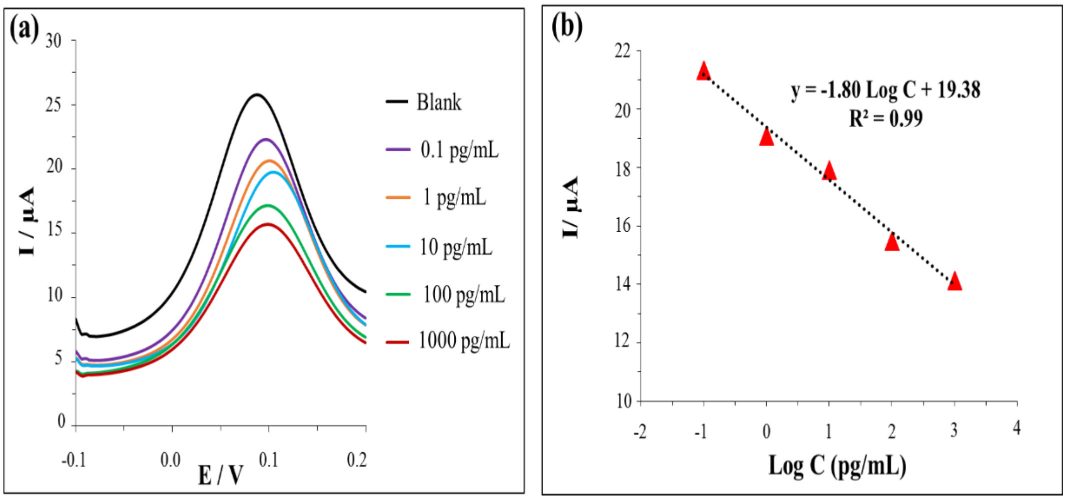

Figure 3. (a) DPV curves of synthetic TCS detection; (b) calibration curve.

3.3. Selectivity, Reproducibility, and Repeatability of the MIP Sensor

It is well-known that the selectivity propriety is an important factor for the implementation of MIP sensors in real sample analysis. Indeed, the outcome proves the excellent selectivity of the MIP sensor for TCS detection.

The reproducibility and repeatability of the MIP sensor was also examined, and the results were good with a relative standard deviation (RSD) less than 4%.

3.4. Application of the MIP Sensor in Real Samples

To study the practicability of the suggested MIP sensor, it was employed for the electrochemical detection of TCS in the spiked wastewater samples. The obtained results are outlined in Table 1. The recovery values were above 99% for all samples with an average RSD less than 6%.

Table 1. TCS content detection by MIP sensor.

Sample	Added (pg/mL)	Found (pg/mL)	RSD (%)
Kasba/ Meknes	0.1	0.08 ± 0.02	0.5
	1	1.06 ± 0.12	2.5
	10	9.66 ± 0.32	5.6
	100	98.83 ± 0.45	0.2
	1000	968.45 ± 0.62	3.7

3.5. Wastewater Samples Spiked with TCS Samples Characterization by E-nose

Wastewater samples spiked with TCS were used for qualitative analysis using the e-nose system.

The Figure 5 illustrate the variation of the maximum conductance (G_s) as a function of time of 6 TGS sensors when exposed to different aliquots of spiked Kasba wastewater sample. We find that all sensors generate a signal that vary heterogeneously when exposed to different concentrations of TCS. Only the TGS 842 sensor shows a homogeneous variation of the conductance. Roughly speaking, the Gs increase with increasing concentrations.

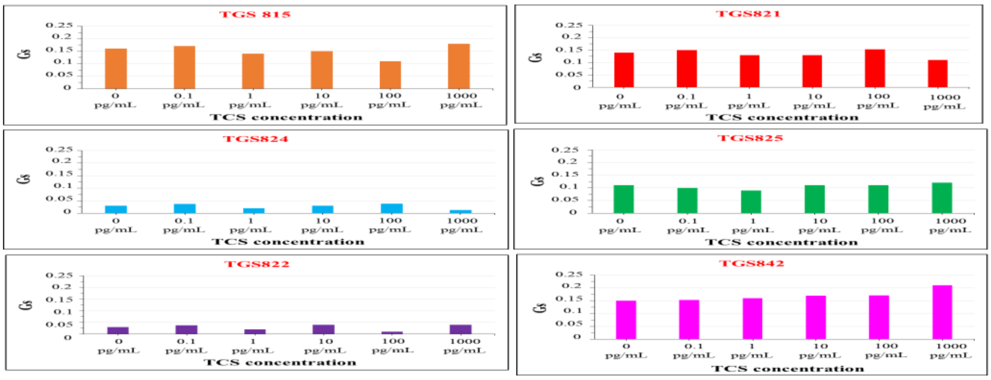

Figure 5. Variation of the maximum sensor conductance after exposure to different concentrations of TCS.

The response of each gas sensor to the samples is displayed in Figure 6 using the radar plot tool. We found that the shape of the radial representations changes with the variation of the TCS concentration in the sample.

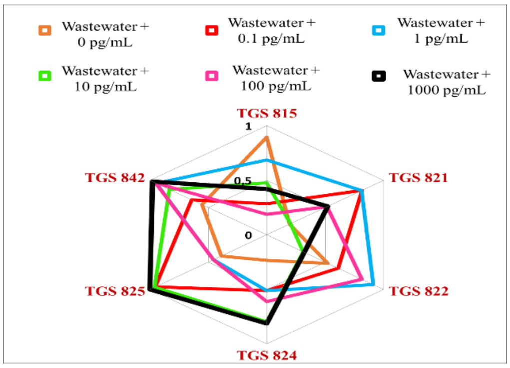

Figure 6. Radar plots of the e-nose responses toward the six wastewater concentrations (using Gs as feature).

3.6. PLS-R regression Results

PLS-R model was constructed by using all the data without separating them into training or validation matrices. The correlation is obtained with R = 0.98 between the predicted concentrations by e-nose and the actual one by MIP sensor as depicted in Figure 7. This allows us to state that the developed e-nose is capable of accurately predicting TCS concentrations in environmental samples.

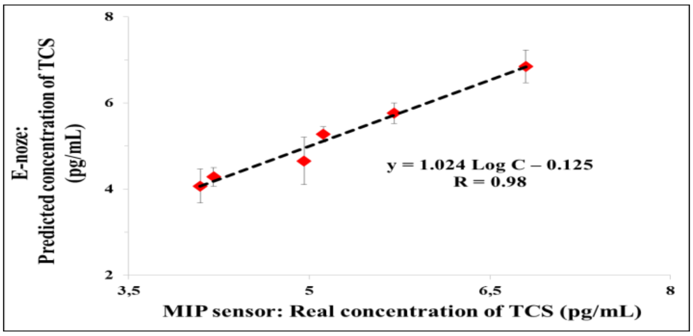

Figure 7. PLS prediction model of TCS content in wastewater samples by means of MIP sensor versus e-nose.

4. Conclusion

In summary, a MIP sensor was successfully designed. It revealed to be highly sensitive and selective for the quantitative analysis of TCS over a wide range with a low detection limit. Moreover, the qualitative analysis performed by the e-nose system was well carried out, and was applied to spiked wastewater samples with very promising results. In addition, good calibration between e-nose and MIP sensor using PLS regression was obtained with a coefficient of correlation (R= 0.98).

Acknowledgments: The authors would like to cordially express gratitude to Moulay Ismaïl University of Meknes for funding the project ''Scientific Research Promotion'' under grant number 2018. The authors would like to thank CNRST-Morocco for the PhD student award of the merit scholarship and the European project "TROPSENSE" under H2020-MSCA-RISE-2014, grant agreement number: 645758.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Duis, K.; Junker, T.; Coors, A. Environmental fate and effects of water-soluble synthetic organic polymers used in cosmetic products. *Env. Sci. Eur.* **2021**, *33*, 1-20.
2. Abidemi, B. L.; James, O. A.; Oluwatosin, A. T.; Akinropo, O.J.; Oraeloka, U. D.; Racheal, A. E. Treatment technologies for wastewater from cosmetic industry—a review. *Int. J. Chem. Biomol.* S **2018**, *4*, 69-80.
3. Mohan, S.; Balakrishnan, P. Triclosan in treated wastewater from a city wastewater treatment plant and its environmental risk assessment. *Water Air Soil Pollut*. **2019**, *230*, 1-13.
4. Rocha, B.A.; de Oliveira, A.R.M.; Barbosa Jr, F. A fast and simple air-assisted liquid-liquid microextraction procedure for the simultaneous determination of bisphenols, parabens, benzophenones, triclosan, and triclocarban in human urine by liquid chromatography-tandem mass spectrometry. *Talanta* **2018**, *183*, 94-101.
5. Kaur, I.; Gaba, S.; Kaur, S.; Kumar, R.; Chawla, J. Spectrophotometric determination of triclosan based on diazotization reaction: response surface optimization using Box–Behnken design. *Water Sci. Technol.* **2018**, *77*, 2204-2212.
6. Zheng, J.; Zhang, M.; Ling, Y.; Xu, J.; Hu, S.; Hayat, T.; Yang, F. Fabrication of one dimensional CNTs/Fe3O4@ PPy/Pd magnetic composites for the accumulation and electrochemical detection of triclosan. *J. Electroanal. Chem.* **2018**, *818*, 97-105.
7. Sanati, A.; Jalali, M.; Raeissi, K.; Karimzadeh, F.; Kharaziha, M.; Mahshid, S.S.; Mahshid, S. A review on recent advancements in electrochemical biosensing using carbonaceous nanomaterials. *Microchim. Acta* **2019**, *186*, 1-22.
8. Raziq, A.; Kidakova, A.; Boroznjak, R.; Reut, J.; Öpik, A.; Syritski, V. Development of a portable MIP-based electrochemical sensor for detection of SARS-CoV-2 antigen. *Biosens. Bioelectron.* **2021**, *178*, 113029.
9. Park, S.Y.; Kim, Y.; Kim, T.; Eom, T.H.; Kim, S.Y.; Jang, H.W. Chemoresistive materials for electronic nose: Progress, perspectives, and challenges. *InfoMat* **2019**, *1*, 289-316.
10. Wu, T.; Li, T.; Liu, Z.; Guo, Y.; Dong, C. Electrochemical sensor for sensitive detection of triclosan based on graphene/palladium nanoparticles hybrids. *Talanta* **2017**, *164*, 556-562.

11. Moreira, F.T.; Dutra, R.A.; Noronha, J.P.; Sales, M.G.F. Surface imprinting approach on screen printed electrodes coated with carboxylated PVC for myoglobin detection with electrochemical transduction. *Procedia Engineering* **2012**, *47*, 865-868.
12. Delgado, D.R.; Holguin, A.R.; Martinez, F. Solution thermodynamics of triclosan and triclocarban in some volatile organic solvents. Vitae **2019**, *19*, 79-92.
13. Motia, S.; Bouchikhi, B.; El Bari, N. An electrochemical sensor based on molecularly imprinted polymer conjointly with a voltammetric electronic tongue for quantitative diphenyl phosphate detection in urine samples from cosmetic product users. *Sens. Actuators B: Chem* **2021**, *332*, 129449.
14. Haddi, Z.; Amari, A.; Alami, H.; El Bari, N.; Llobet, E.; Bouchikhi, B. A portable electronic nose system for the identification of cannabis-based drugs. *Sens. Actuators B: Chem*. **2011**, *155*, 456-463
15. Liang, R.; Kou, L.; Chen, Z.; Qin, W. Molecularly imprinted nanoparticles based potentiometric sensor with a nanomolar detection limit. *Sens. Actuators B: Chem*. **2013**, *188*, 972-977.