Electrochemical Identification of Endocrine-Disrupting Phenols and their Complex Mixtures in Real Samples using Square Wave Voltammetry

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INTRODUCTION

Phenolic endocrine disrupting chemicals (EDCs) are commonly found in wastewater due to their wide use as surfactants, plasticizer, dyes and disinfectants [1,2]. Exposure to these toxic, bioaccumulable and persistent EDCs can have adverse effects as they interfere with the endocrine system [3,4]. Unfortunately, to date, there are no strict regulations and control on the discharge of the EDCs in our environment. Hence, there is an urgent need for better detection methods based on highly sensitive and selective user-friendly sensors for on-site application. For this reason, we present for the first time a comprehensive work including the study of the electrochemical behavior of a selection of the most relevant phenolic EDCs, i.e., phenol (PHOH), pentachlorophenol (PCP), 4-tert octylphenol (OP) and bisphenol A (BPA) in Britton Robinson (BR) buffer using unmodified carbon screen-printed electrodes (SPEs) and square wave voltammetry (SWV).

RESULTS

A. OPTIMIZATION OF ELECTROCHEMICAL APPROACH

1. Stability study of phenols over time using different storage conditions.

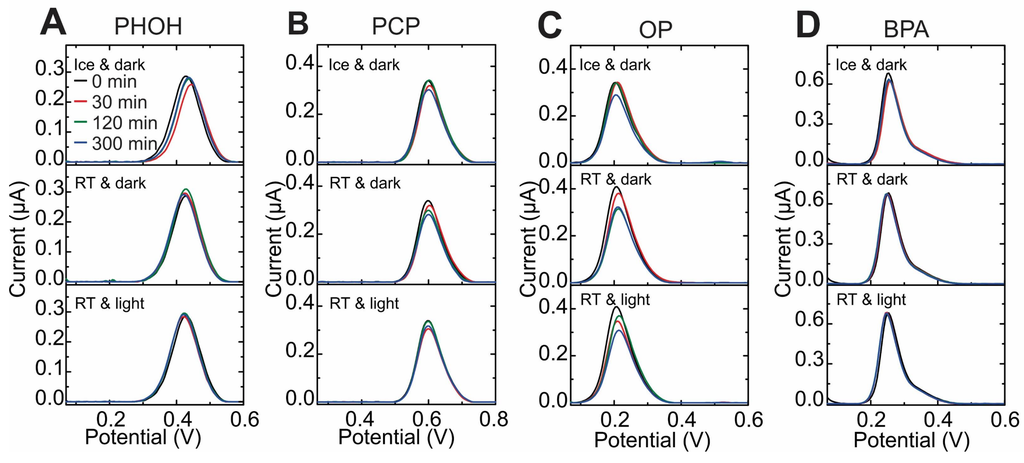

Fig. 1. Baseline corrected square wave voltammograms of 10 µM phenols in pH 12 BR buffer, A) PHOH, B) PCP, C) OP and D) BPA. Stability of different stocks over the time (from 0 till 5 hours) stored in ice and dark; at room temperature (RT) and dark; and at room temperature and daylight.

2. Anodic pretreatment for the degradation of phenol over time.

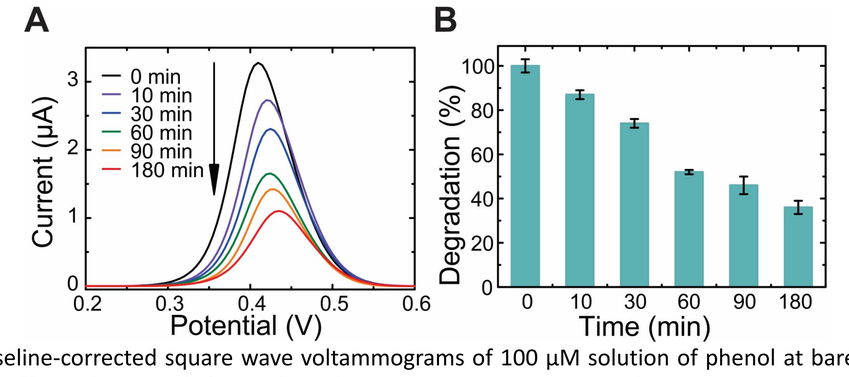

Fig. 2. Baseline-corrected square wave voltammograms of 100 µM solution of phenol at bare carbon SPE in pH 12 BR buffer with a straightforward anodic pretreatment at 0.9 V (N=3).

3. Analytical performance of the SPE during calibration curves of phenols.

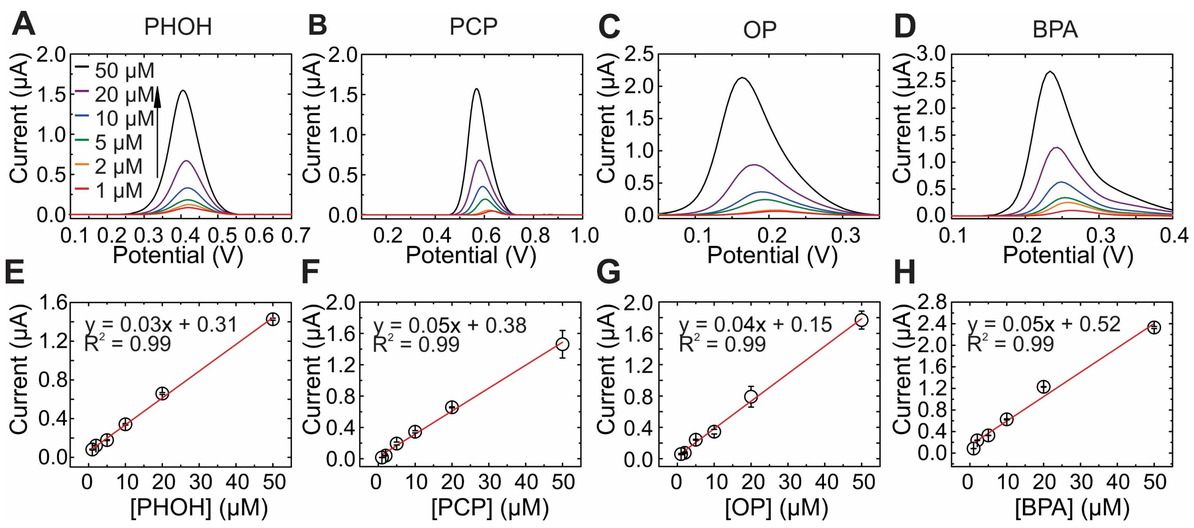

Fig. 3. Baseline corrected square wave voltammograms for A) PHOH, B) PCP, C) OP and D) BPA in pH 12 BR buffer in a concentration range from 1 to 50 µM using bare carbon SPE (N=3).

4. Selective identification of all phenols in complex mixtures.

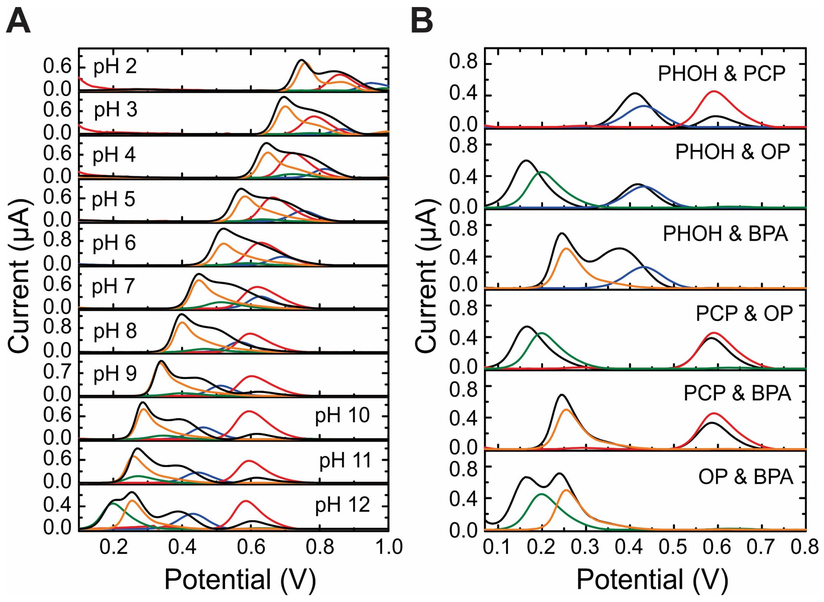

Fig. 4. Baseline corrected square wave voltammograms obtained after A) pH screening (pH 2 to 12) in BR buffer of complex mixture (black line) using 10 µM concentration of each phenol (1:1:1:1 ratio) and B) binary mixture of phenols (black line) of 10 µM concentration of each phenol (1:1 ratio) in pH 12. Single phenol solutions of PHOH (blue line), PCP (red line), OP (green line) and BPA (orange line) also provided.

B. VALIDATION OF ELECTROCHEMICAL APPROACH

5. Determination of phenols in real samples (Scheldt river water) by SWV and validation with HPLC-DAD technique.

.	SWV	HPLC-DAD	
Sample	**Recovery (%)**	**Recovery (%)**	**Accuracy (%)**
PHOH	110.32 ± 0.45	102.29 ± 0.05	107.86
PCP	103.23 ± 1.54	101.42 ± 0.03	101.79
OP	88.19 ± 4.80	110.21 ± 0.30	80.02
BPA	108.76 ± 1.41	107.25 ± 0.05	101.41

Table 1. Recovery values obtained from the spiked Scheldt river samples of individual phenols in 10 µM concentration in pH 12 BR buffer for SWV and ultrapure water for HPLC-DAD, and the accuracy values between the electrochemical approach and the standard technique, HPLC-DAD (N=3).

CONCLUSION

- ✓ Rapid voltammetric detection method is used for an in-depth electrochemical study of four different highly relevant endocrine-disrupting phenols using unmodified carbon SPEs.
- ✓ The different phenols showed remarkable stability at pH 12 in BR buffer under different types of storage conditions.
- ✓ The application of an anodic pretreatment allowed degradation of phenol over time.
- ✓ The performed calibration curves showed the analytical performance of the SPEs and their capability for the accurate identification of different phenols in complex mixtures simultaneously based on their unique electrochemical fingerprint.
- ✓ Validation with real samples and comparison with lab-bench standard method (HPLC-DAD) allowed that the electrochemical approach is demonstrated for providing rapid and reliable screening of phenols in real samples during on-site testing.

FUTURE WORK

The advances presented in this article will pave the way for the development of a new generation of electrochemical sensors allowing simultaneous identification of phenolic EDCs in a portable device aiming at on-site detection of phenols in industrial processes and/or wastewater.

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