Targeted, suspect and non-targeted liquid chromatography - high resolution mass spectrometry for identification of degradation products of selected pollutants in water samples

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Introduction

The presence of organic pollutants such as pharmaceuticals, drugs, pesticides, personal care products and many others, in various parts of the environment is an actual global problem. Moreover, within these complex samples, many chemicals remain unidentified or emerge through various biotic and abiotic degradation and/or transformation processes of their parent compounds and may cause adverse effects to aquatic organisms at very low concentration e.g. especially endocrine disruption [1]. The presence of persistent pollutants in the environment is associated with the risk of adverse effects on living organisms and therefore new treatment technologies are intensively studied.

Boron doped diamond electrodes (BDDEs) belong to the EAOPs, technologies based on the generation of highly reactive oxidizing species, typically hydroxyl radicals (•OH), that are able effectively degrade different types of organic pollutants [2, 3]. In this context, a combination of liquid chromatography and high-resolution mass spectrometry (LC-HRMS), allows the identification and quantification of many known and unknown compounds due to its high resolution, accuracy, and selectivity. The identity of all contaminants can be elucidated in three main workflows by target analysis, suspect screening, and non-target screening [4].

Aims of work

- **2D and 3D BDD electrodes for highly effective, ecological and safe removal of selected pollutants from water**
- **LC-MS/MS analysis for evaluation of efficacy of treatment process**
- **Suspect and non-target screening using LC-ESI-HRMS for identification of degradation and transformation products of selected persistent pollutants**

Experimental

Analytical standards of selected pollutants were obtained from Sigma-Aldrich. Electrochemical oxidation was performed with different types of BDDE 2.5% CH_4/H_2 10,000 ppm B/C on structured, non-structured silicon substrate and porous ceramics (40 ppi). Degradation experiments were realized in deionized water with the addition of the selected pollutant (c = 1 mg/L) and also with salts addition (NaCl or Na_2SO_4). Samples were taken by an automatic dosing system at characteristic time intervals (0; 30; 60; 120; 240 minutes). The collected samples were filtered through regenerated cellulose filters with a pore size of 0,45 µm.
The model and wastewater samples from the degradation experiments were analyzed by LC-MS/MS using the triple quadrupole mass analyzer TSQ Quantiva (Thermo Fisher Scientific, USA) with heated electrospray on positive and negative ionization mode. Identification of degradation products was performed by LC-HRMS instruments, LC-MS-IT-TOF™ (Shimadzu) and QExactive (Thermo Fisher Scientific). Compound Discoverer 3.3 (Thermo Fisher Scientific) with workflows containing retention time alignment, peak detection, accurate m/z (<5 ppm) elemental composition calculation, halogens isotope pattern detection and statistical analysis were used for data processing.

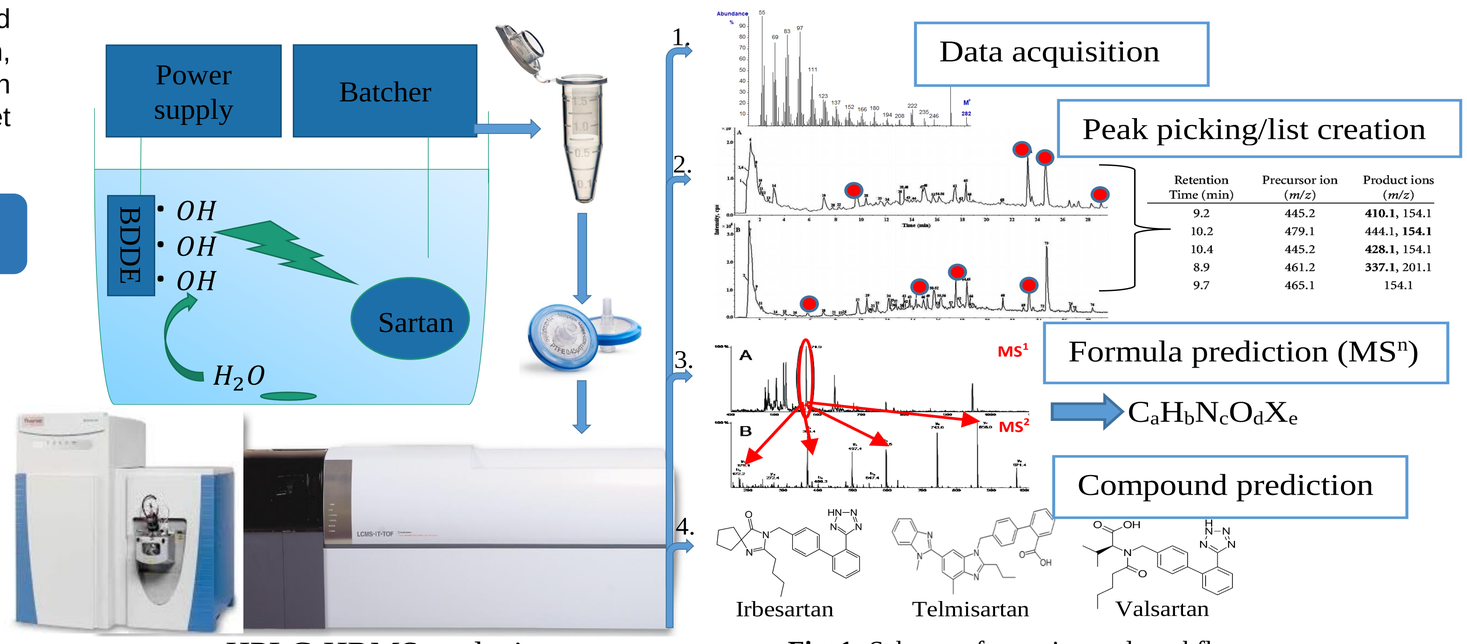


Fig. 1: Scheme of experimental workflow

Results and discussion

ELECTROCHEMICAL OXIDATION ON BDDE AND TARGETED ANALYSIS

The effect of using different types of BDDE and different salt of working electrolyte on the different type of pollutants (pharmaceuticals, pesticides, azofarbives) removal efficiency was studied.

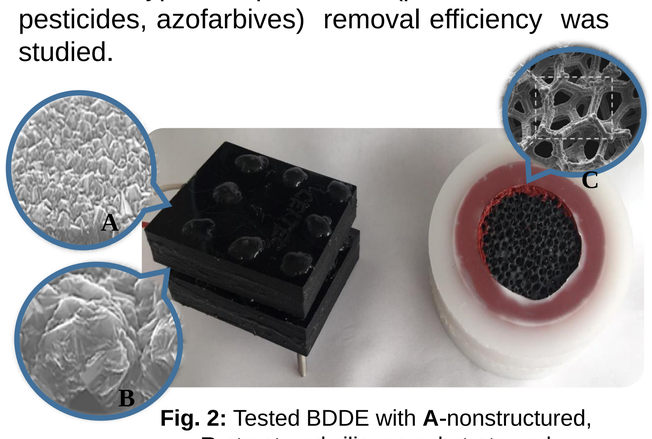


Fig. 2: Tested BDDE with **A**-nonstructured, **B**-structured silicone substrate and **C**-3D porous ceramics

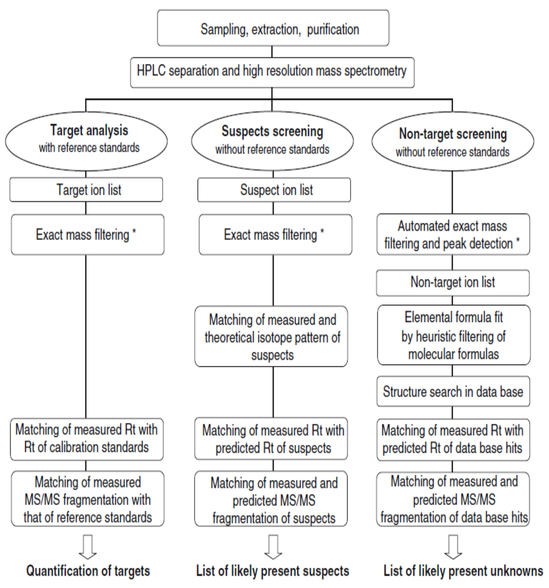


Fig. 3: Schematic view of LC-HRMS approaches in environmental analysis

The choice of electrolyte, specifically the salt used in the reaction, plays a crucial role in determining the efficiency of electrochemical oxidation, particularly for selected pharmaceuticals. We observed a significant increase in the elimination efficiency of all selected pharmaceuticals when NaCl was used as the electrolyte across all tested electrodes, while the different electrode morphologies did not lead to significant differences in the removal rates (see in Tab. 1).

Tab. 1: The removal efficiency of pharmaceuticals on different BDDE in NaCl after 240 minutes of treatment.

Analyte	Si/BDD	sSi/BDD
Carbamazepine	38.6	99.5
Diclofenac	99.7	99.6
Irbesartan	98.8	99.1
Telmisartan	96.3	98.1
Trimethoprim	84.5	99.9
Venlafaxine	54.3	99.9

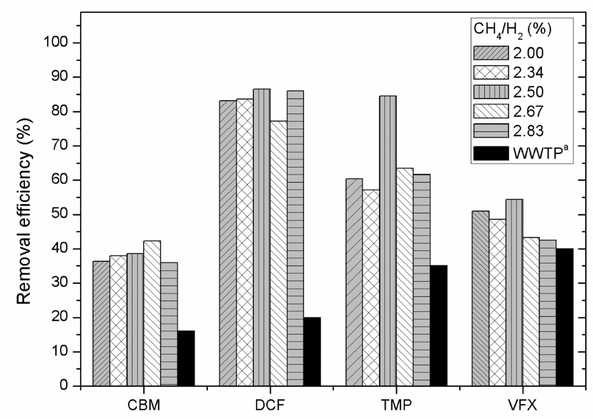


Fig. 4: The elimination on selected pharmaceuticals in wastewater on different BDDE

The obtained results can be explained by generation of reactive chlorine species contributing to pharmaceuticals degradation.
Using BDDEs was possible to remove hardly degradable pharmaceuticals with better efficiency than is average WWTP removal.

SUSPECT ANALYSIS NON-TARGETED ANALYSIS

Suspect analysis focuses on compounds that are expected based on sample data. To identify the suspect compounds, we had created a list of already published degradation products. The list summarizes all the data that contribute to more efficient searching (peak selection) and preliminary identification (m/z in ESI (+/-), fragment ions in MS^2 stage, summary and structural formula).
Non-targeted approach of identification is characterized by absence of available preliminary information about the nature, structure or molecular weight of the analytes. The non-targeted analysis mainly involves the design of the molecular formula of unknowns based on high-resolution MS^1 and MS^2 data.

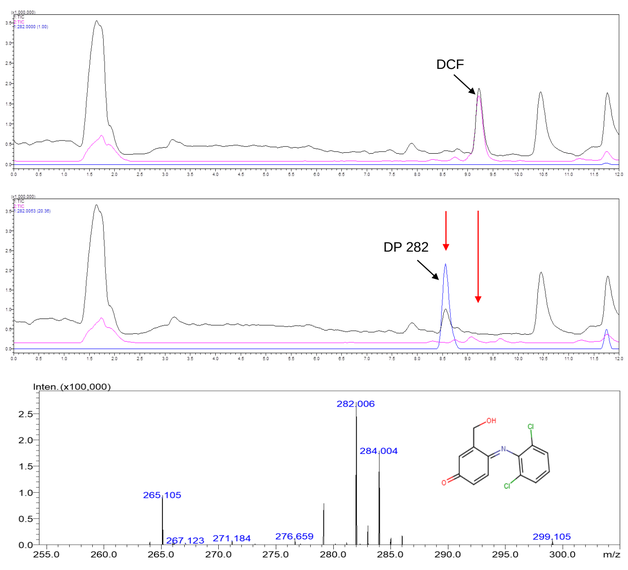


Fig. 5: The creation of suspect degradation product of diclofenac and its mass spectrum

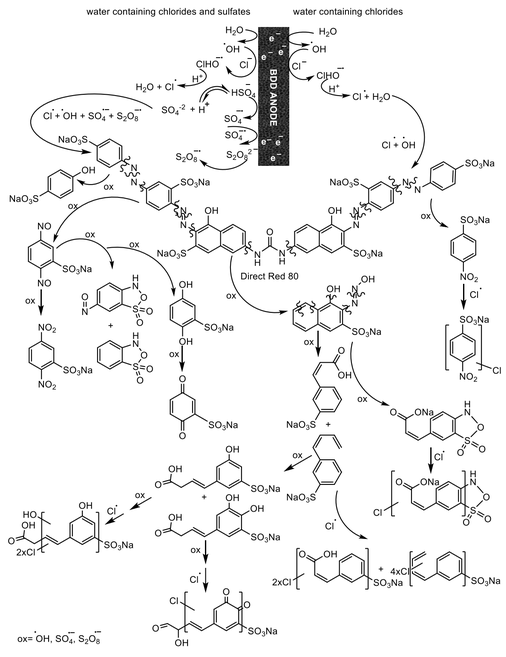
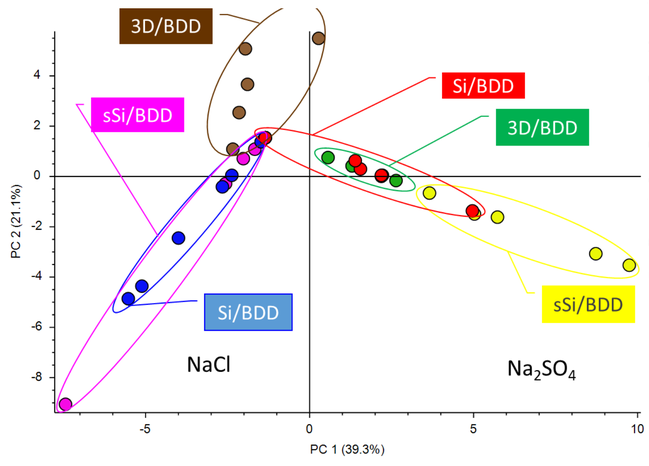


Fig. 6: Proposed degradation pathway of Direct Red 80 in the presence of chlorides and sulfates.



To investigate the differences or similarities in formation of chlorinated DCF transformation products among all tested combinations, we applied PCA analysis of nontargeted datasets. The signals were filtered to keep only chlorine-containing molecules (Cl, Cl2, Cl3, Cl4)

Fig. 7: PCA plots of the data obtained by electrochemical oxidation of DCF in different combinations of BDD electrodes and supporting electrolytes.

Conclusion

- ✓ An approach to the effective removal of pollutants using different types of BDDE and electrolyte has been proposed.
- ✓ The target LC-MS/MS analysis for evaluation of elimination efficiency was used.
- ✓ The suspect and non-targeted LC-HRMS for identification of degradation and transformation products was successfully applied

REFERENCES [1] P. Šauer, et al., Environment International 178 (2023) 107957, [2] E. Mordačiková, et al J. Electroanal. Chem. 862 (2020) 114007, [3] Y. Jiang, et al., Electrochem. Commun. 123 (2021) 106912, [4] J. Hollender, et al., Environ. Sci. Tech. 51 (2017) 11505.

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