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Unravelling the mechanisms of organic micropollutant removal in bio-electrochemical systems: Insights into sorption, electrochemical degradation, and biodegradation processes

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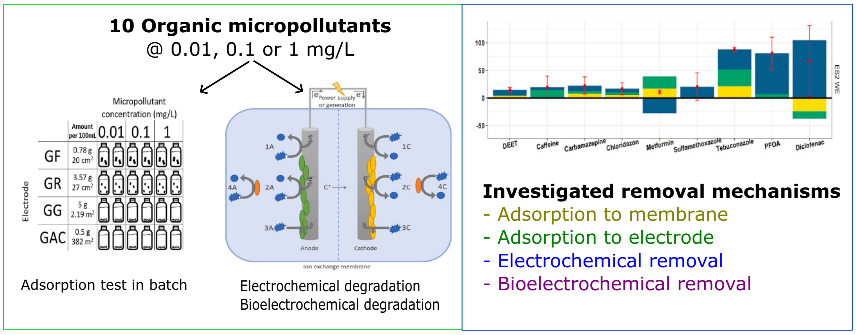
HIGHLIGHTS

- This manuscript distinguishes between sorption and electrochemical/biological degradation.
- Sorption was lowest for graphite felt electrodes.
- Removal efficiencies >80 % were obtained at high anode potentials (+0.955 V).
- For most micropollutants, biofilm impeded sorption and/or degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Bio-electrochemical systems (BESs) have recently been proposed as an efficient treatment technology to remove organic micropollutants from water treatment plants. In this study, we aimed to differentiate between sorption, electrochemical transport/degradation, and biodegradation. Using electro-active microorganisms and electrodes, we investigated organic micropollutant removal at environmentally relevant concentrations, clarifying the roles of sorption and electrochemical and biological degradation. The role of anodic biofilms on the removal of 10 relevant organic micropollutants was studied by performing separate sorption experiments on carbon-based electrodes (graphite felt, graphite rod, graphite granules, and granular activated carbon) and electrochemical degradation experiments at two different electrode potentials (−0.3 and 0 V).

Granular activated carbon showed the highest sorption of micropollutants; applying a potential to graphite felt electrodes increased organic micropollutant removal. Removal efficiencies >80 % were obtained for all micropollutants at high anode potentials (+0.955 V), indicating that the studied compounds were more susceptible to oxidation than to reduction. All organic micropollutants showed removal when under bio-electrochemical

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conditions, ranging from low (e.g. metformin, 9.3 %) to exceptionally high removal efficiencies (e.g. sulfamethoxazole, 99.5 %). The lower removal observed under bio-electrochemical conditions when compared to only electrochemical conditions indicated that sorption to the electrode is key to guarantee high electrochemical degradation. The detection of transformation products of chloridazon and metformin indicated that (bio)-electrochemical degradation occurred. This study confirms that BES can treat some organic micropollutants through several mechanisms, which merits further investigation.

1. Introduction

Organic micropollutants are a diverse group of anthropogenic chemicals including pharmaceuticals, hormones, personal care products, pesticides, surfactants, and industrial chemicals. Organic micropollutants can be recalcitrant to degradation and threaten environmental and human health, despite their presence at trace concentrations (ng/L to μg/L) (Luo et al., 2014; Meyer et al., 2019). Many contaminants and/or their transformation products are discharged via the effluent to surface water (Farré et al., 2008; Talib and Randhir, 2016). The presence of organic micropollutants is a challenge for water reuse practices within the transition towards a circular economy (Guerra-Rodríguez et al., 2020; Voulvoulis, 2018).

Bio-electrochemical systems (BESs) have been proposed as a treatment technology to prevent or minimize the release of organic molecules into the aquatic environment. BESs provide a unique environment in which microorganisms can use electrodes as electron donor or acceptor, catalysing the conversion of chemical energy into electric energy and vice versa. This relies on the decoupling of an oxidation reaction, happening at the anode, from a reduction reaction, happening at the cathode. When working with bio-anodes, the biofilm, which is composed of electro-active bacteria, oxidizes organic substrates, releasing electrons that flow towards the cathode, where they are used to reduce electron acceptor, such as oxygen. In the case of bio-cathodes, energy is invested to split water at the anode and to generate electrons that will be used in the reduction reaction catalysed by the biofilm at the cathode (Bajracharya et al., 2016; Hamelers et al., 2009). This versatility places BES as a very interesting system to investigate organic micropollutant degradation and the removal mechanisms.

In a practical perspective, BESs also show advantages in comparison to the already existing treatment technologies used to remove organic micropollutants. These include advanced oxidation processes (Rodriguez-Narvaez et al., 2017), activated carbon adsorption (Nam et al., 2014; Piai et al., 2020), membrane filtration (Luo et al., 2014; Rodriguez-Narvaez et al., 2017), and constructed wetlands (Rodriguez-Narvaez et al., 2017). However, these treatments are often energy intensive, can produce toxic transformation products or concentrated waste streams, require a large surface area and operation time, and/or have high investment, operation and maintenance costs (Luo et al., 2014). In contrast to the aforementioned technologies, BESs demand little to no energy, require little maintenance, and do not generate concentrated waste streams. Hence, BESs avoid high operational costs and are considered sustainable, which makes their implementation more attractive compared to other advanced technologies (Chakraborty et al., 2020).

Recent research has shown that many types of BES configurations can be applied to remove single or specific groups of organic micropollutants, including dyes (Chakraborty et al., 2020), antibiotics (Yan et al., 2019; Zhang et al., 2020), and monoaromatic compounds (Yang et al., 2020). In general, these BESs are studied with either anodic or cathodic organic micropollutant removal, and the other chamber contains a chemical solution to drive the counter-reaction. For example, Zhang et al. (2020) observed high removal (70–90 %) for antibiotic sulfamethoxazole in the anodic chamber, whereas Wang et al. (2015a) obtained 78 % and 73 % removal of caffeine and carbamazepine, respectively, in the cathodic chamber. Nevertheless, it is crucial to gain a comprehensive understanding of the underlying mechanisms responsible for removal and to differentiate between the processes that collectively contribute to organic micropollutant removal. Fig. 1 highlights the following four main processes in the anodic (A) and cathodic (C) chamber (Wang et al., 2015b):

1. Electrochemical degradation: organic micropollutants can be oxidized (1 A) or reduced (1C) at the anode or cathode without catalysis by the electroactive biofilm.
2. Bio-electrochemical degradation: organic micropollutants can be oxidized (in the anode, 2 A) or reduced (in the cathode, 2C) by the electro-active microorganisms in a biofilm. The electrodes serve as electron acceptor or donor, respectively.
3. Sorption: organic micropollutants can sorb to the electrodes or biofilm (3 A,C). Sorption processes include physical or electrode potential-induced sorption (i.e. electro-sorption).
4. Biodegradation: organic micropollutants can be biodegraded by planktonic (i.e. free-living) microorganisms suspended in the anolyte or catholyte (4 A,C). These planktonic microorganisms use dissolved species as electron acceptor (e.g., oxygen) or donor (e.g., hydrogen) rather than electrodes.

To exploit BESs full potential as a sustainable treatment technology that effectively degrades organic micropollutants, it is imperative to understand the fate of such molecules in various BES configurations. This requires testing the sorption of organic micropollutants on different electrode materials and membranes in bio-electrochemical reactors. Evaluating oxidation and reduction potentials for electrochemical removal and examining transformation product formation during biological degradation are necessary. Typically, graphite and carbon-based electrodes, such as granular activated carbon (Yan et al., 2023) and felt (Sun et al., 2022) have been used as bioanode, due to their high specific surface area and stability. However, the relationship between biofilm development on anode and micropollutants removal has not thoroughly been explored, partially due to the challenging experimental setup required. While the use of visual techniques that allow to monitor growth and composition of biofilm on anodes in real time could bring added value to the field of micropollutants removal in BESs (Pereira et al., 2022a).

Despite recognition in environmental reviews (Fernando et al., 2018), reporting on essential mechanisms for substantiating organic micropollutant degradation in BES research is lacking. In addition, there is necessity of establishing a connection between research and practical application. This involves investigating how operational parameters, such as applied potential, affect removal, as well as exploring the impact of organic micropollutants mixtures at environmentally relevant concentrations.

Here, the removal of 10 organic molecules at the bioanode of a double chamber BES using environmentally relevant concentrations was studied. Sorption tests to different electrode materials were performed, the oxidation and reduction potentials of the analysed organic micropollutants were calculated, and by analysing transformation compounds, novel insights into the role of electrochemical and bio-electrochemical degradation mechanisms in BESs were obtained. Together, this research provides a strong foundation for further investigation into organic micropollutant removal in BESs.

2. Methodology

2.1. List of organic micropollutants and growth medium

A mixture of 10 organic micropollutants with different physical and chemical properties was used in this study (Table 1). These compounds were selected to represent a range of organic pollutants commonly found in wastewater and surface water, exhibiting a spectrum of physical, chemical, and environmental persistence characteristics. All chemicals were ordered from Sigma-aldrich and were of pharmaceutical secondary standard or analytical standard. Using UPLC-MS quality acetonitrile, a mixture organic micropollutant solution containing 100 mg/L of each chemical was prepared from 1 g/L organic micropollutant individual stock acetonitrile solutions. All (mixed) organic micropollutant stock solutions were stored in glass amber bottles at −20 °C.

The growth medium used in this experiment contained 2 mM potassium acetate and was buffered by a triphosphate buffer at pH 7.3–7.4. In addition, the medium contained 10 mL/L macronutrient solution, 2 mL/L micronutrient solution, and 1 mL/L vitamin solution as described in Ter Heijne et al. (2008). All solutions were prepared in Milli Q ultrapure water and stored at 4 °C.

2.2. Abiotic organic micropollutants sorption in batch

Batch experiments of four days were performed to analyse the sorption of organic micropollutants to different electrode materials that are commonly used in BESs: graphite felt (GF), graphite rod (GR), graphite granules (GG), and granular activated carbon (GAC). These electrode materials were selected based on their diverse range in surface area and sorption capacity, their conductivity, biocompatibility and chemical stability. For each electrode material, sorption was tested at three initials organic micropollutants concentrations: 0.01, 0.1 and 1 mg/L. The electrode material and organic micropollutant concentration that showed the lowest removal of organic micropollutants was chosen for the follow-up experiments in electrochemical and bioelectrochemical conditions.

Three bottles with growth medium (Section 2.1) were prepared, each spiked with the 100 mg/L organic micropollutant stock mix (Section 2.1) to obtain a concentration of either 0.01, 0.1 or 1 mg/L for each individual compound. In addition, solvent concentration was equalised in every batch. As only sorption was intended to be studied in these experiments, 20 mM sodium azide and 1.1 mM mercury chloride were added to inhibit aerobic and anaerobic microbial activity, respectively. Final volume in the serum bottles (250 mL) was of 100 mL of medium.

The electrodes were pre-treated before to be placed in the serum bottles. Graphite felt, GF, (CGT Carbon GmbH, Asbach, Germany) was cut into pieces of 2x5cm and weighed to verify that the pieces had the same area. Graphite rods, GR, were broken into pieces of approximately 1 × 1.5 cm and weighed in packages of 3.57 g (±0.1 g) each to ensure equal surface area for each batch. Graphite granules, GG, (Carbone Lorraine Benelux BV, Wemmel, Belgium) were rinsed with demineralized water for 5 min and dried before use. Granular activated carbon, GAC, (PK1–3, Cabot Norit Nederland BV, Amersfoort, The Netherlands) was washed for 1 h with demineralized water and then boiled in demineralized water for 2 min to remove entrapped air from the pores (Piai et al., 2019). The electrodes were placed in the batches based on representative electrode to liquid ratios for each material obtained from literature; GF = 2 cm^2/L, GR = 2.7 cm^2/L, GG = 0.219 m^2/L and GAC = 38.2 m^2/L (Bond and Lovley, 2003; Chen et al., 2010; Elzinga et al., 2020; Piai et al., 2019, 2020; Zhang et al., 2010) (Supplementary information Fig. S1). All serum bottles were closed with a rubber stopper, wrapped in aluminium foil, and placed on a shaker at 135 RPM and room temperature for four days.

At the start of the sorption tests and every 24 h, three 1 mL samples were taken. Samples were centrifuged at 15,000 rpm for 10 min and the supernatant was transferred to a clean LC-vial before to be store at −20 °C until analysis. The t_0 samples were taken from the three bulk solutions of organic micropollutants at different concentrations, and the t_1 samples were taken from the same solutions immediately after introducing the electrode materials to the bottles. All experiments were performed in duplicate.

Organic micropollutant sorption to the membrane was tested following the same procedure as described above for the electrode materials. Bipolar membrane (2.2 cm × 2.9 cm, fumasep® FBM-PK,

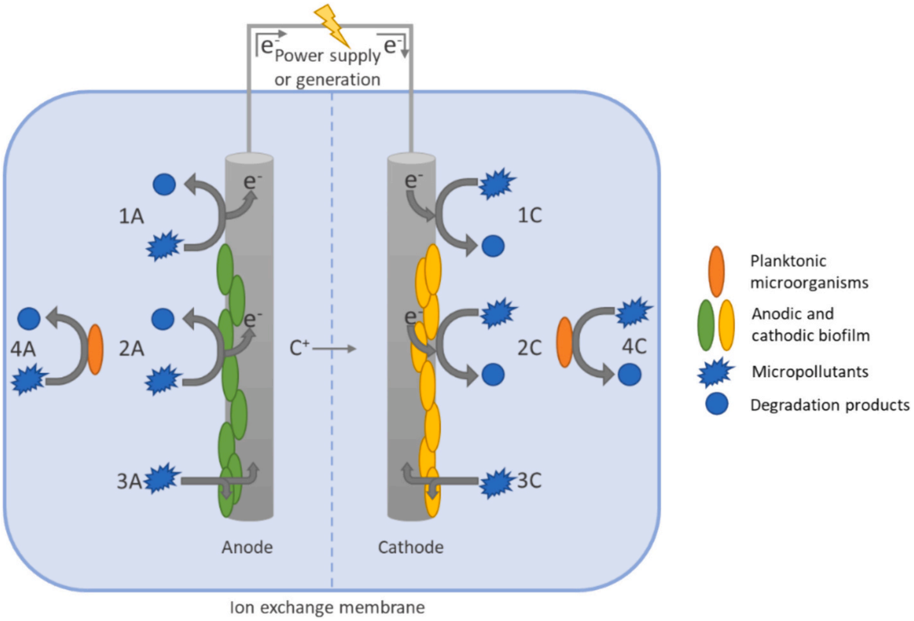

Fig. 1. Schematic overview of a BES showing the main organic micropollutant removal mechanisms that can occur in the anodic or cathodic chamber. 1 A,C: Anodic or Cathodic electrochemical oxidation or reduction; 2 A,C: Anodic or Cathodic bioelectrochemical oxidation or reduction; 3 A,C: Sorption to the biofilm-covered Anode or Cathode; 4 A/C: Planktonic biodegradation in the Anodic or Cathodic chamber. C^+ represents a cation passing the membrane to maintain charge neutrality. Note: in practice, organic micropollutants will be introduced either to the anode or cathode, and the other chamber will contain a chemical solution suitable for the counter reaction.

Table 1
List of organic micropollutants used in this study, their Log D_{OW} and oxidation (E_{OX}) and reduction (E_{RED}) potentials (expressed as V vs Ag/AgCl). Details on the calculation of the redox potentials can be found in Supporting Information, S1(theoretical oxidation and reduction potentials for benzotriazole, carbamazepine and chloridazon are unknown).

Organic micropollutant or *Transformation product*	CAS number	Class	Log D_{ow}^{k} at pH 7.3	E_{OX}	E_{RED}
PFOA (Perfluorooctanoic acid)	335–67-1	Industrial chemical	−1.19	−1.593	0.104
Benzotriazole	95–14-7	Industrial and household chemical	1.44	N.A.	N.A.
Caffeine	58–08-2	Food and drug additive	−0.07	−0.272	−0.042
DEET	134–62-3	Pesticide	2.18	−0.467	−0.183
Chloridazon	1698-60-8	Pesticide and herbicide	−2.78	N.A.	N.A.
Desphenyl-chloridazon	6339-19-1	Transformation product			
Methyldesphenyl- chloridazon	17,254–80-7	Transformation product			
Tebuconazole (DMI, 3)	107,534–96-3	Pesticide and fungicide	3.70	−0.490	0.040
Diclofenac	15,307–86-5	Pharmaceutical	1.36	−0.584	−0.117
Metformin	1115-70-40	Pharmaceutical	−7.74	−0.048	0.317
Guanylurea	141–83-3	Transformation product			
Sulfamethoxazole	723–46-6	Antibiotic	−0.28	−0.402	−0.080
Carbamazepine	298–46-4	Pharmaceutical	2.45	N.A.	N.A.

Fumatech BWT GmbH, Bietigheim-Bissingen, Germany) was placed in the serum bottles filled with medium spiked with organic micropollutants at either 0.01, 0.1, or 1 mg/L.

2.3. Electrochemical and bio-electrochemical organic micropollutant removal

H-cells were used to perform the electrochemical (ES) and bio-electrochemical (BES) micropollutants removal experiments that are detailed in Sections 2.3.1 and 2.3.2. The anode and cathode chambers were separated with the same bipolar membrane as the one tested in the sorption experiments. The cation exchange side was facing the counter electrode and the anion exchange side was facing the working electrode, to keep a neutral pH in both the anode and cathode compartments and to minimize the transport of compounds between the two chambers. Graphite felt was selected as electrode material for the ES and BES experiments, since it showed the lowest removal efficiency in the sorption experiments (see Section 3.1).

Graphite felt (CGT Carbon GmbH, Asbach, Germany) of 0.4 cm × 4.4 cm × 8.4 cm was used for both the working electrode and counter electrode, being electrically connected using a platinum wire (used as current collector). The graphite felt was non-microporous with a surface area < 1 m^2/g, as determined by N_2 physisorption (de Smit et al., 2024).

A 3 M KCl Ag/AgCl reference electrode (+0.205 V vs NHE, Prosense, Oosterhout, the Netherlands) was inserted in the chamber containing the working electrode and a potentiostat (Ivium, The Netherlands) was used to perform chronoamperometric measurements, with the potential control at the working electrode and monitoring of produced current every 60 s. To guarantee anoxic conditions, the liquid phase in both anode chamber (the anolyte) and cathode chamber (chamber) was flushed with nitrogen gas for 30 min before the start of the ES and BES experiments. Besides, during the experiments, the chambers were gently sparged with nitrogen gas when oxygen concentration raised above 2 %. Oxygen concentration was measured in both chambers using Oxydots (Oxygen Sensor Spot SP-PSt6-NAU, PreSens, Germany).

Each chamber had an internal volume of approximately 350 mL. The H-cells were operated at room temperature (22 °C), stirred at 200 RPM and shielded from light with aluminium foil. All conditions were tested in duplicate.

2.3.1. Electrochemical system experiment

Four double-chamber electrochemical systems (ESs, BES without electrode biofilm) were constructed for four days to analyse the influence of electrode potential on organic micropollutant removal.

Each chamber was filled with 300 mL medium spiked with 100 mg/L organic micropollutant mix to obtain a concentration of 0.01 mg/L. Similar to the sorption experiments (Section 2.2), the medium (Section 2.1) used in the ES experiments contained 20 mM sodium azide and 1.1 mM mercury chloride to inhibit biological activity. The working electrodes of two electrochemical systems were controlled at −0.3 V vs Ag/AgCl and the working electrodes of the other two electrochemical systems were controlled at 0 V vs Ag/AgCl. These potentials were selected based on thermodynamic calculations (Table 1) and aimed at allowing for the oxidation of the organic micropollutants used in this study. Every 24 h, two 1 mL samples were taken from the anolyte and catholyte of each electrochemical system. Samples were centrifuged at 15,000 rpm for 10 min and the supernatant was transferred to a clean LC-vial before to be store at −20 °C until analysis. The t_0 samples were taken from the bulk solution and the t_1 samples were taken immediately after introducing the medium (with 0.01 mg/L of organic micropollutants) to the chambers. Anolyte and catholyte pH were measured at the start and end of the experiment, which lasted four days.

2.3.2. Bio-electrochemical system experiment

Two H-cells were constructed to investigate organic micropollutant degradation at a bio-anode over 30 days.

Before the addition of organic micropollutants, BESs were operated for 36 days to promote formation of an electro-active biofilm on the anode, hereafter referred to as acclimation period. The anode chambers were inoculated with 15 mL anaerobic granular sludge from a paper industry wastewater treatment plant (Eerbeek, The Netherlands). The microorganisms were fed with the growth medium without the mixture of organic micropollutants (total liquid volume of 315 mL), and the anodes were controlled at −0.3 V vs Ag/AgCl. The chambers of the counter electrode (cathode) were filled with a 50 mM solution of potassium hexacyanoferrate (III) in 20 mM potassium phosphate buffer at pH 7.3–7.4, to allow studying the bio-anode without interfering effects of a limiting reduction reaction at the cathode. Organic micropollutants were only part of the composition of the anolyte to be able to target biological removal, and to avoid interfering reduction reactions of organic micropollutants at the cathode. When the current dropped below 0.5 mA, approximately 250 mL of the anolyte was replaced with fresh medium to circumvent substrate limitations. During the acclimation period for anodic biofilm formation (that lasted for 36 days), the duplicate BES reactors generated a maximum current density of 0.084 mA/cm^2 (3.1 mA) in BES 1 and 0.092 mA/cm^2 (3.4 mA) in BES 2. After the two BESs produced similar current profiles for over 3 cycles of medium replacement, it was assumed that an active biofilm was established at the anode.

To start the organic micropollutant biodegradation tests, the growth medium (315 mL) including suspended cells was removed from the chamber and replaced with fresh medium spiked with 100 mg/L organic micropollutant mix to obtain a starting concentration of 0.01 mg/L of each compound. Only the biofilm attached to the surface remained in the chamber. In the cathode chambers, the hexacyanoferrate (III) solutions in phosphate buffer were also replenished. Anolyte and catholyte were purged with nitrogen gas to remove eventual oxygen that penetrated in the chambers during the replacement of the anolyte and catholyte. After 30 min of nitrogen sparging, the anode was controlled at −0.3 V vs Ag/AgCl. The BESs were operated for 30 days after addition of the organic micropollutants. Daily anolyte samples were taken (two times 1 mL) for organic micropollutant quantification. As described previously, samples were centrifuged at 15,000 rpm for 10 min and the supernatant was transferred to a clean LC-vial before to be store at −20 °C until analysis.

Anolyte and catholyte pH were measured at the start, middle and end of both the acclimation period and the organic micropollutant removal experiment. Toxicity of the micropollutants at the tested concentration (0.01 mg/L) was not controlled in this study. However, information found in the literature shows that none of them should be expected to exhibit toxic or inhibition effect at this concentration (Table S1C).

2.4. Analysis

2.4.1. Organic micropollutants quantification

Organic micropollutant concentrations, including transformation products (Desphenyl-chloridazon, methyldesphenyl-chloridazon and guanylurea), were quantified only in the liquid phase with liquid chromatography coupled to a tandem mass spectrometry (LC-MS/MS) using a Shimadzu LC20 connected to a Sciex Triple Quad 5500+. The analysis was limited to the liquid phase due to the presence of heterogeneous adsorbent materials and electrode materials used in both batch and BES tests.

After sampling, 1 mL samples were centrifuged for 10 min at 15,000 RPM after which the supernatant was transferred to an amber LC injection vial. Samples were stored at −20 °*C. prior* to analysis, samples were diluted to 1 μg/L in 95 % ultra-pure water and 5 % acetonitrile and stored at 4 °C until injection in the LC-MS/MS. Calibration standards were prepared in a range of 0.02 to 1 μg/L in 95 % ultra-pure water and 5 % acetonitrile.

Chromatographic separation was performed on a reversed phase LC column (1.7 μm particle size, 150 × 2.1 mm, phenyl-hexyl 100 Å, Kinetex©). The column oven temperature was set at 35 °C and the injection volume was 25 μL. The mobile phase consisted of solvent A: ultrapure water with 0.1 % formic acid, and solvent B: acetonitrile with 0.1 % formic acid. Two pumps were used to create a gradient of solvent A and B for 10 min with a flow rate of 0.4 mL/min. All test compounds were ionized in positive mode, except for PFOA and diclofenac, which were ionized in negative mode. Details on the established LC-MS/MS methods and parameters of the multiple reaction monitoring to identify and quantify the organic micropollutants are shown in Supporting Information S2. The quantification limit in matrix of the method was 20 ng/L while the detection limit in matrix was not measured in this project. AB SCIEX Analyst and SCIEX OS-MQ software were used for data acquisition and analysis.

2.4.2. Data processing

Data analyses and figures production were performed using Excel, R (vers. 4.0.2) and the R package ggplot2 (vers. 3.3.5).

Organic micropollutant removal in relative concentration over time were calculated with the following equation:

$$C_t \Big/ C_0\% = \frac{C_t}{C_0} * 100\% \qquad (1)$$

where C_0 is the initial concentration measured in the sample from the bulk solution (mg/L) and C_t is the final concentration in the liquid (mg/L).

The total removal consisted of sorption to membrane and electrode, and removal due to (bio)degradation. The total micropollutant removal in the BES was thus corrected for sorption to the membrane and the electrode, which were calculated from the batch test results obtained in the sorption experiments.

3. Results and discussion

3.1. Sorption of organic micropollutants to electrode materials

Batch sorption tests at three different organic micropollutant concentrations revealed large differences in organic micropollutant sorption to the electrode materials and the membrane (Fig. 2). Conversely, metformin, tebuconazole, diclofenac, and caffeine demonstrated strong adsorption across nearly all tests, indicating a high affinity for the studied materials. Despite diclofenac and tebuconazole being hydrophobic and metformin and caffeine being hydrophilic, the adsorption equilibrium was unaffected by the hydrophobicity of the micropollutants. However, the adsorption kinetics (see Supporting Information, Fig. S3) may be influenced by this parameter (Nam et al., 2014), but this was not further investigated in this study.

The materials with high sorption efficiency (>40 %) were the granular activated carbon (96 ± 5 %) and graphite granules (55 ± 28 %).

The lowest sorption efficiency was observed for graphite felt (8 ± 13 %). The sorption to the membrane was also low, and for most organic micropollutants, similar to sorption to the graphite felt (13 ± 16 %). The observed removal reflects the total organic micropollutant removal for the typical electrode-to-liquid volume ratios used in BESs. The trends were similar for all organic micropollutants, irrespective of their physical-chemical properties, which is in line with other studies (Nam et al., 2014; Piai et al., 2019; Werner et al., 2015). For some chemicals, such as diclofenac and metformin, higher starting concentration often resulted in higher absolute values for sorption to activated carbon and graphite granules (see Supporting Information, Fig. S3 for all concentration profiles).

However, for some other compounds, such as DEET and chloridazon, lower sorption efficiencies to graphite felt and membrane were obtained when higher starting concentrations were used. This is likely to be related to the saturation of these electrode materials resulting in low sorption efficiencies compared to the efficiencies obtained when lower organic micropollutants concentrations were used.

Finally, sorption is a relevant removal mechanism that should be considered when selecting (B)ES reactor materials. To better distinguish the removal driven by ES and BES from sorption-based removal, graphite felt electrode was selected for the (B)ES experiments since it combined the least removal by sorption with the highest surface area.

3.2. Electrochemical sorption and degradation of organic micropollutants

The removal of organic micropollutants in an electrochemical cell, in the absence of microorganisms, was studied under a controlled anode potential of −0.3 and 0 V vs Ag/AgCl. At −0.3 V vs Ag/AgCl, the measured current at the anode was approximately −0.14 mA, a factor 100 more negative than the current measured when the anode potential was controlled at 0 V vs Ag/AgCl (∼ -1.4×10^{-3} mA). For both conditions, the potential of the counter electrodes (CE) was more positive than the potential applied to the working electrode (WE): for the WEs controlled at −0.3 V vs Ag/AgCl, the counter electrode potentials were + 0.9 and + 1.0 V vs Ag/AgCl, and for the WE controlled at 0 V vs Ag/AgCl, the counter electrode potentials were + 0.4 and + 0.5 V vs Ag/AgCl.

Differences in organic micropollutant removal efficiency were found between CE and WE and among the electrode potentials tested (Fig. 3). In general, the organic micropollutants with high removal efficiency (>40 %) were sulfamethoxazole, tebuconazole, PFOA and diclofenac. Components that were moderately removed (20–40 %) were caffeine, carbamazepine, metformin and chloridazon. Low removal (10–20 %)

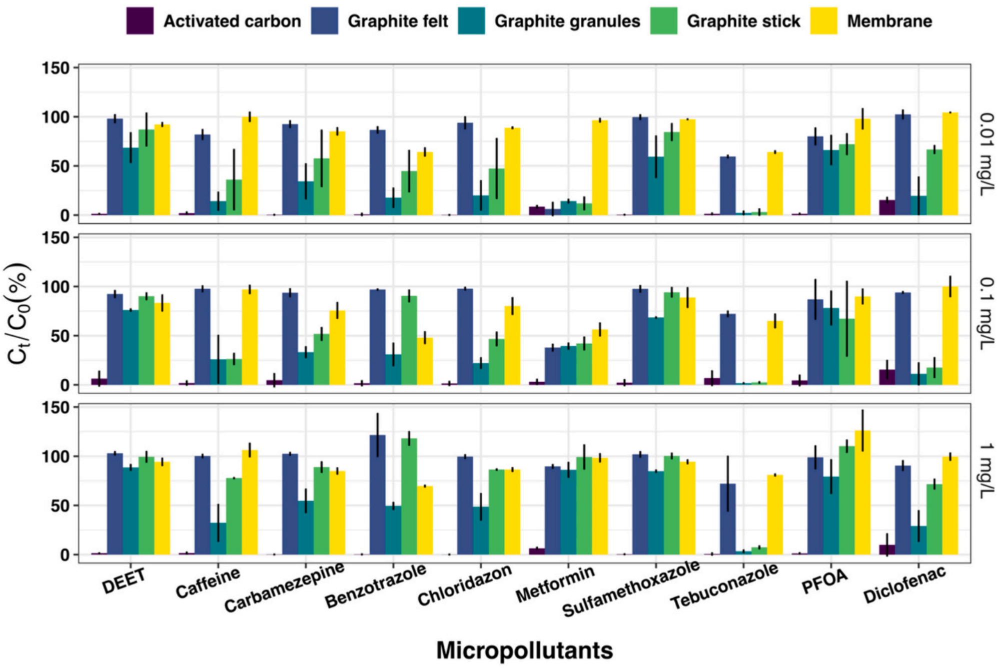

Fig. 2. Removal (in relative concentration, %) of studied organic micropollutants by sorption to the different electrode materials and to the membrane used in the (B)ES reactors. Error bars represent the standard deviation between replicates ($n = 2$).

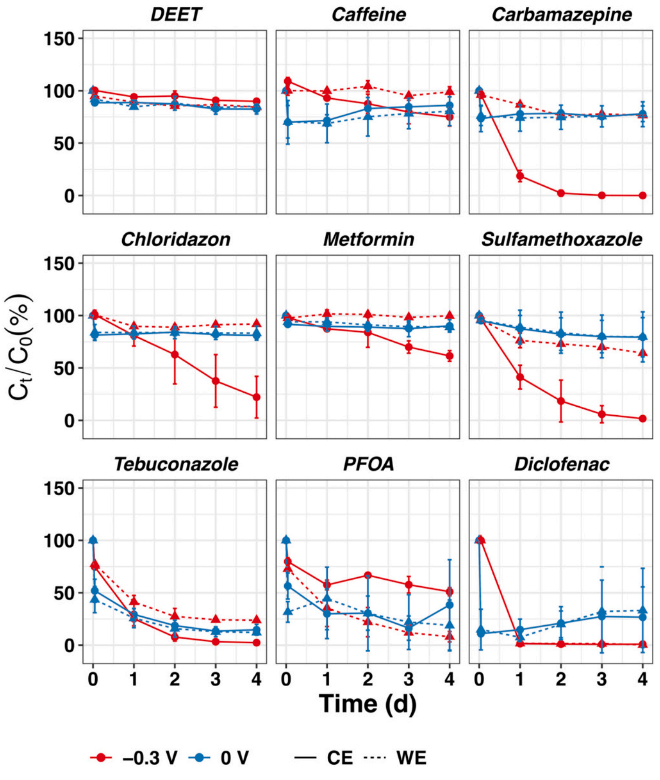

Fig. 3. Concentration gradients of the studied organic micropollutants in the chamber of the working electrode (WE, triangle symbol) and counter electrode (CE, circle symbol) in the electrochemical systems in which the WE were controlled at −0.3 V (red) and at 0 V (blue). Average concentrations are shown for the duplicates, and error bars show the standard deviation. Data for benzotriazole are not showed due to instrumental error during this analysis, leading to an inaccurate quantification of this specific compound.

was found for DEET.

More organic micropollutant removal was achieved when using a WE with a more negative current compared to the WE set at 0 V vs Ag/AgCl (Fig. 3). This enhanced removal was particularly notable for carbamazepine, chloridazon, metformin, sulfamethoxazole, and diclofenac. Some of these compounds, such as diclofenac, exhibited an extremely rapid decline in concentration within the initial hours of the batch process, indicating their swift adsorption and degradation in the electrochemical system.

Considering the consistent decrease in organic micropollutant concentration observed in both the anode and cathode compartments of the electrochemical system, we can disregard removal associated with transport through the bipolar membrane. Moreover, transport through the membrane is improbable because a bipolar membrane, which obstructs the passage of both positively and negatively charged species, was employed. Based on Table 1, most organic micropollutants included in this study were more susceptible to be removed by oxidation as opposed to reduction. The thermodynamic potentials show that electrochemical oxidation of all tested compounds could occur at all counter electrodes, since the thermodynamic potentials were lower than the measured counter electrode potentials (+0.4, +0.5, +0.9, and + 1.0 V vs Ag/AgCl). At a WE potential of −0.3 V vs Ag/AgCl, electrochemical reduction of all organic micropollutants could occur since the thermodynamic potential was higher than the controlled potential. However, at a WE potential of 0 V vs Ag/AgCl, electrochemical reduction could only occur for some organic micropollutants: electrochemical reduction was not thermodynamically possible for DEET, caffeine, diclofenac, and sulfamethoxazole, as the thermodynamic potentials were more negative than the applied electrode potential. This indicates that the removal of those organic micropollutants in the WE controlled at 0 V vs Ag/AgCl could be attributed to sorption.

Desphenyl-chloridazon, a degradation product of chloridazon, was found in all chambers proving that partial degradation of chloridazon occurred. The only exception was observed in the CE chamber of the H-cell in which the WE was controlled at 0 V vs Ag/AgCl, in which no desphenyl-chloridazon was detected. Interestingly, electrochemical degradation produces this same transformation product as biodegradation (Buttiglieri et al., 2009).

As expected, higher potential, at the CE, enhanced oxidation while lower potential, at the WE, enhanced organic micropollutant reduction (Cui et al., 2009; Guo et al., 2017; Kong et al., 2015, 2017). No consistent correlation between the log D_{OW} of the studied chemicals (Table 1) and their removal efficiency in the different ESs was observed. The same holds true for the findings obtained in the sorption experiments. For instance, DEET removal was slow and limited under all studied conditions, whereas its relatively high log D_{OW} (2.2) would suggest high sorption. Exceptions were rapid and good removal of tebuconazole, and slow and poor removal of metformin at the WE and CE of both ESs. This was in accordance with their high (3.7) and low log D_{OW} (−7.7), respectively.

In addition to electrochemical removal, another reason for the observed removals could be linked to electrostatic interactions. When a potential is applied, electrostatic interactions can enhance or impede sorption of charged organic micropollutants to the electrode and membrane (Bayram et al., 2009; Bayram and Ayranci, 2010; Divyapriya et al., 2020). In the present study, the relationship between organic micropollutant charge and removal in the ESs was not always consistent. For example, the negative potential of the WE controlled at −0.3 V vs Ag/AgCl was expected to result in electrostatic repulsion of the negatively charged diclofenac, sulfamethoxazole and PFOA, impeding sorption and electrochemical removal. Similarly, electrostatic attraction between the positively charged metformin and the WE controlled at −0.3 V vs Ag/AgCl was expected to enhance removal. However, the opposite trend was observed for this WE, with relatively high removal of negatively charged organic micropollutants and low removal of metformin compared to their removal under more positive electrode potentials.

3.3. Bioelectrochemical removal of organic micropollutants

After the acclimatization phase used to grow a mature electro-active biofilm on the WE, biological degradation of the organic micropollutants under anodic conditions were tested for 30 days.

We are considering that our biofilm system was stable throughout the test period. In BES studies, biofilms and electrodes are generally studied throughout a period of weeks, months, or even years. Even though biofilm conversions and BES performance may fluctuate, due to variations in wastewater composition, generally, BES can be operated for long time periods in a stable way. In other examples, even though we used a different type of electrode in the present study, the biofilm grew and remained attached to the biofilm for approximately 30 days under different anode potential and feeding conditions (Pereira et al., 2022b).

Removal at the bio-anodes was observed for all organic micropollutants, exhibiting a wide range of removal efficiencies from 9.3 to 99.5 % (Fig. 4). High removal efficiencies (>40 %) were obtained for sulfamethoxazole, tebuconazole, diclofenac and benzotriazole. Compounds that were moderately removed (20–40 %) were chloridazon, caffeine and carbamazepine. DEET showed the lowest removal (10–20 %). However, it should be noted that low removal (<10 %) of DEET could be the result of measurement inaccuracies, as acknowledged by the OECD biodegradability tests (OECD, 2006). Metformin showed moderate removal (40 %) especially after day 20, however this was not observed in the replicate experiment. Reproducible removals were obtained for the other organic micropollutants, with maximum variances between duplicates within the range of 15–30 % for the removal efficiencies of diclofenac, sulfamethoxazole, and benzotriazole.

At the anode potential of −0.3 V vs Ag/AgCl used in these experiments, the oxidation of DEET, diclofenac, sulfamethoxazole, and tebuconazole was thermodynamically favourable (> 0.102 V overpotential, see Table 1). DEET is known to exhibit a low sorption tendency, as shown in Fig. 3 (Bernhard et al., 2006; Dos Santos et al., 2019), while it was partially removed in BES, suggesting (bio)electrochemical degradation. The removal of sulfamethoxazole showed the highest efficiency, confirming that bio-electrochemical degradation was dominant over sorption (Miran et al., 2018; Wang et al., 2016).

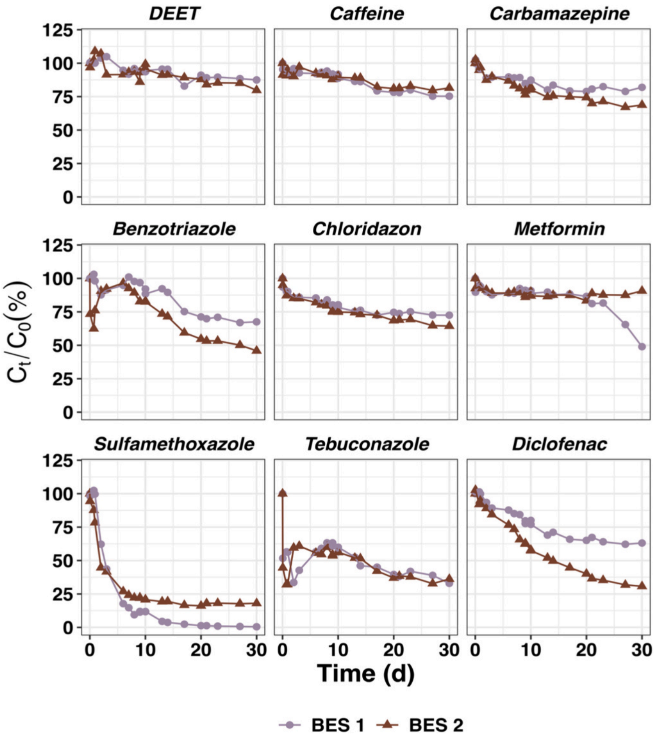

Fig. 4. Removal (in relative concentration, %) of the studied organic micropollutants at the bio-anode of the BES. Duplicates are shown for each organic micropollutant. PFOA data are not shown because the results were inconsistent, potentially due to matrix effects.

In addition to biological oxidation with the electrode as electron acceptor, also microaerophilic biodegradation in the anode chamber due to oxygen contamination in the anode chambers may have played a role. For example, the observed removal of caffeine, with a thermodynamic oxidation potential of −0.272 V vs Ag/AgCl and metformin (−0.048 V vs Ag/AgCl), could be due to oxygen intrusion into the anode chambers, as neither reaction was thermodynamically favourable. Low oxygen levels in the anodic chamber were detected (0.16–5.2 %) and could be used as an alternative final electron acceptor and play a role in aerobic biodegradation of organic micropollutants in the anolyte. Since caffeine is known to be easily biodegradable (Tran et al., 2013; Werner et al., 2015), the contribution of aerobic biodegradation to caffeine removal in the anolyte cannot be neglected. Detection of trace concentrations of guanylurea, desphenyl-chloridazon and methyldesphenyl-chloridazon (below quantification limit) indicated that metformin and chloridazon were (bio)degraded to some extent. In addition, the enhanced metformin biodegradation in one replicate after day 20 could be related to prolonged substrate limitation. Since metformin can be biologically degraded without presence of co-substrate (A. Dalmijn et al., 2021; Briones et al., 2018; Poursat et al., 2019), estimated acetate depletion in the medium may have led to a shift from the use of acetate to the use of metformin as carbon and energy source for biological activity.

There was no clear link between the removal of organic micropollutants and the current generated in the BES (see Supporting Information, Fig. S4). After acclimation, in the first few days after organic micropollutant feeding, produced current peaked around 0.091 mA/cm^2 (2 mA) and slowly decreased after. After nine days, the addition of fresh acetate and phosphate buffer led to a rapid increase in current density to a maximum of 0.11 mA/cm^2 (2.6 mA), which dropped again and remained low until day 30. This low and decreased produced current was mostly influenced by the depleting acetate concentrations rather than by the influence of the organic micropollutants, which is not expected to be relevant given the low organic micropollutant concentrations used.

3.4. *The interplay between sorption and (bio)electrochemical degradation*

Total removal is a combination of sorption to the electrode material and membrane, (electro)sorption, electrochemical degradation, membrane adsorption and bio-electrochemical degradation. Fig. 5 shows the bio-electrochemical removal and the electrochemical removal for each organic micropollutant. Here, the electrochemical removal is fractioned into two parts: electrosorption and electrochemical removal. Since both electrosorption and electrochemical conversion determine the organic micropollutant removal in electrochemical experiments, electrochemical removal is defined as the sum of the contributions of these two processes.

Fig. 1 For all organic micropollutants except metformin, electrochemical removal enhanced removal compared to sorption. For metformin, sorption was higher than the total removal in the ESs, hence the negative sign for electrochemical degradation. This suggests that applying a potential to the GF electrode impedes the removal of metformin, which may be related to metformin carrying a positive charge at neutral pH.

Overall, the total removal was similar for both WEs in the ES experiments, meaning that there was no considerable effect of the applied potential (0 or - 0.3 V vs Ag/AgCl) on organic micropollutant removal. However, from these ES experiments, it becomes clear that an applied potential does enhance removal compared to sorption alone onto the electrode material. (Electro)sorption could enhance electrochemical degradation due to an increased local concentration of organic micropollutant in the boundary layer of the electrode or hinder electrochemical degradation due to repulsion that results in a decreased availability of reaction sites. Whether and how the applied potential influences organic micropollutant (electro)sorption and/or degradation remains poorly understood and is often overlooked.

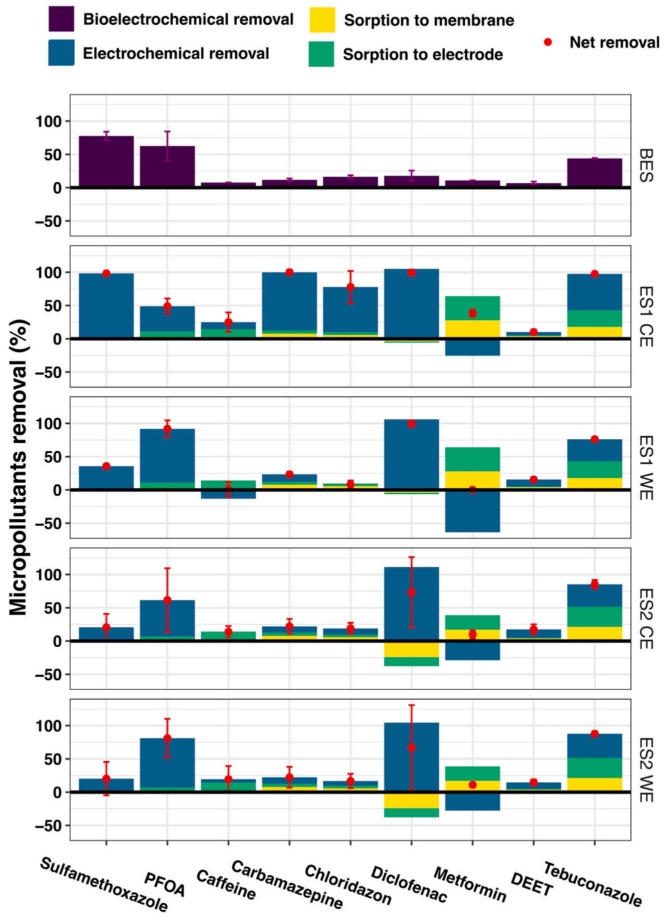

Fig. 5. Organic micropollutant removal in BES in the ES systems, for both WE and CE. Stacked bars include sorption to the membrane (yellow), sorption to the GF electrode (green) determined from the sorption experiments, and the (remaining) electrochemical removal (blue). The net removal is indicated with red dots. Data for benzotriazole are not shown due to instrumental error during this analysis, leading to an inaccurate quantification of this specific compound.

A comparison between organic micropollutant removal in the ES and BES experiments shows that the removal efficiency for all compounds (in the first 6 days) was generally higher for the ES than for to the BES (Fig. 5). Concentrations in the WE chamber of the BESs reached equilibrium after 10 days or later (Fig. 4), whereas most chemicals had reached equilibrium concentrations by day 4 in the WE chamber of the ESs. The presence of a biofilm on the electrode may lower the sorption and/or electrochemical degradation because of slower diffusion of organic micropollutants through the biofilm, and because of lower sorption properties to biofilms compared to electrodes (Joss et al., 2005; Kowalska et al., 2019; Mazioti et al., 2015). Continued decrease in concentrations in the BESs after day 4 suggests that bio-electrochemical degradation did result in additional removal of DEET, caffeine, carbamazepine, diclofenac, tebuconazole and benzotriazole.

Chloridazon, metformin, and sulfamethoxazole were the only organic micropollutants with similar or higher removal efficiencies in the BESs compared to the ESs, except for the CE chamber of the ES experiment in which the WE was controlled at −0.3 V vs Ag/AgCl. In addition, removal of chloridazon, metformin, and sulfamethoxazole is higher in the BES experiments compared to their removal observed at the (abiotic) CE. However, the electrode potential in CE was more positive (+0.5 V vs Ag/AgCl) in comparison to the −0.3 V vs Ag/AgCl used in the BES experiments, suggesting that the presence of a biofilm stimulated removal by reducing the overpotential needed to drive the degradation of these organic micropollutants, working thus as a (bio)-catalyst. Besides, it is unlikely that this removal was caused by sorption to the biofilm-covered electrodes, given the high hydrophilicity of the organic micropollutants (negative log D_{OW}, Table 1).

Several organic micropollutants we used here have also been studied before in BES, in which a wide range of removal efficiencies and conditions are reported without further analysis of the removal mechanisms. For DEET, diclofenac and carbamazepine, moderate removal was reported for anodic removal in a BES (Wang et al., 2015c), which agrees with the results reported in Fig. 5. Regarding sulfamethoxazole, high removal efficiencies reported in other studies are coherent with the results reported here (Miran et al., 2018; Wang et al., 2016; Wang et al., 2015c). Interestingly, higher caffeine removals have been reported in other studies when compared to the removals reported here (Wang et al., 2015c; Werner et al., 2015). A possible explanation could be the co-metabolism between (bio)transformation of caffeine and anodic acetate oxidation (Wang et al., 2015c; Werner et al., 2015), which was eventually inhibited due to acetate depletion in the anolyte. Therefore, the low acetate concentration in the anolyte is likely to explain the lower caffeine removal.

4. Conclusion and outlook

This study aimed at distinguishing the organic micropollutant removal mechanisms occurring in BESs and their dependency on electrode material, applied potential and presence of a microbial community. Our insights into the role of sorption (physical and (electro) sorption) and degradation (bio- and electrochemical) in the overall removal of organic micropollutants in BESs pave the way for further research into quantifying different removal mechanisms occurring in BESs.

Whereas electrode properties (e.g. type and material) are fundamental for overall performance of BESs, research into comparing various electrode materials for organic micropollutant removal is limited

(Hassan et al., 2021; Yan et al., 2019). It was here hypothesized that sorption would lead to transport limitations and organic micropollutant accumulation in the system (Wang et al., 2015b; Werner et al., 2015), whereas elevated local concentrations on the electrode surfaces due to sorption may potentially facilitate (bio)electrochemical degradation, as was previously observed in GAC sorption processes (Piai et al., 2021). This interplay between sorption and degradation at different electrode materials merits further investigation, to decipher the dependency of organic micropollutant sorption to the electrode on (bio)electrochemical degradation in BESs.

The effect of the electrode potential on the composition and activity of the microorganisms present in the biofilm attached to the electrode, and consequently, how the potential can be used to steer the BES towards increased organic micropollutant degradation, remains poorly understood (Tahir et al., 2019; Yan et al., 2019; Zhang et al., 2020). Beyond BES being a powerful scientific research tool to better understand biological conversions, this combination of electrodes and biofilms may benefit decentralized approaches towards a better understanding of all the organic micropollutant removal processes occurring. A key research focus is the calculation of redox potentials of organic micropollutants in actual conditions. It is known that the conversion of substrate by the biofilms results in the accumulation of protons in the biofilm, which consequently increases the oxidation potential of the organic micropollutants. Measuring the pH in situ could explain the conversions observed in this work when these were thermodynamically not feasible. Lastly, monitoring transformation products and being able to relate these to organic micropollutants degradation could help close the balance and give insights into the fractions that are removed by sorption and (bio)electrochemically.

Overall, the outcomes of this study demonstrate that BESs are a promising cutting-edge technology to remove organic micropollutants by providing a toolbox of mechanisms. In the long term, the results from this study provide valuable information to improve BES performance for effective degradation regarding different operational parameters. This would greatly assist the development and implementation of full-scale BES technologies for sustainable treatment of organic micropollutants in real WWTP effluent.

CRediT authorship contribution statement

Baptiste A.J. Poursat: Writing – review & editing, Visualization, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Fleur Rempe:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **João Pereira:** Writing – review & editing. **Nora B. Sutton:** Writing – review & editing, Supervision, Resources, Project administration, Formal analysis, Conceptualization. **Annemiek ter Heijne:** Writing – review & editing, Supervision, Resources, Project administration, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary Figures and Tables

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.173932.

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