Retention of Organic Micropollutants in Nutrient Recovery from Centrate by Electrodialysis – Influence of Feed pH and Current Density

Supporting Information

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Chemicals and Analytical Standards

Ultrapure water was produced with a Merck MilliQ Integral 5 System (Merck, Darmstadt, Germany) and used for dilution of all samples, including samples for salts, nutrients and metals analysis. Additionally, it was used for the mobile phase component A in the LC-MS/MS gradient. As mobile phase component B UPLC grad methanol (BioSolve, Valkenswaard, Netherlands) was used.

For analysis of micropollutants by LC-MS/MS, stock solutions of analytical standards were prepared in methanol or a water/methanol mix and stored at -20 °C until calibration standards were prepared. For ICP-MS analysis a mix of analytical standards (Spex 1, Spex 2a, Spex 3, Spex 4; SpexCertiprep, Metuchen, USA) & Merck VI;(Merck, Darmstadt, Germany) was prepared for calibration in an aqueous 1 % HNO_3 (HNO_3 (60%), Ultrapur, Merck, Darmstadt, Germany) solution. Single-element analytical standards for elemental analysis with ICP-OES were obtained from Merck (Darmstadt, Germany) as well.

Tables

Tab. SI 1: Information on operation of electrodialysis system.

parameter	unit	Experiments		
		Varying Current Density	Varying feed pH: Synthetic Feed	Treatment of nitrified centrate
cell pairs ED	-	10	10	10
channel length	mm	110	110	110
channel width	mm	110	110	110
channel thickness	mm	0.45	0.45	0.45
membrane thickness	µm	100-120	100-120	100-120
flow rates	L/h	35-45	45-65	75
flow velocity	m/s	0.20 - 0.25	0.25 - 0.36	0.42
unit cell voltage	V	4 - 6	4 - 6	4 - 6
current	A	0.1; 0.13; 0.11; 0.31	0.2	0.2

Tab. SI 2: Characteristics of nitrified centrate produced by the first stage of the nutrient recovery system investigated in this study. Data is based on unpublished research.

	Nitrified Centrate
TN (mg/L)	880±64
NO_3-N (mg/L)	860±53
PO_4-P (mg/L)	34±1.7
NH_4-N (mg/L)	4.8±2.4
NO_2-N (mg/L)	1.1±0.95
TCOD (mg/L)	180±11
pH (-)	6.0±0.2

Tab. SI 3: Overview of relevant physical chemical properties for analysed micropollutants. Prediction of compound properties by ChemAxon.

	CAS	Mass	$pK_{a,1}$	$pK_{a,2}$	$pK_{b,1}$	$pK_{b,2}$	Isoelectric Point	$logD_{(pH\ 3.0)}$	$logD_{(pH\ 6.0)}$	$logD_{(pH\ 8.0)}$
4/5-Methylbenzotriazole	29878-31-7	133.154	9.3	-	0.5	-2.5	4.9	1.8	1.8	1.8
Acesulfame	33665-90-6	163.15	3.0	-	-6.0	-	-	-0.8	-1.5	-1.5
Benzotriazole	95-14-7	119.127	8.6	-	0.6	-9.6	4.6	1.3	1.3	1.2
Carbamazepine	298-46-4	236.274	16.0	-	-3.8	-	-	2.8	2.8	2.8
Candesartan	139481-59-7	440.463	3.5	5.9	1.5	-1.4	2.5	5.2	2.5	0.3
Diclofenac	15307-86-5	296.15	4.0	16.4	-2.1	-	-	4.2	2.3	0.9
Ibuprofen	15687-27-1	206.285	4.9	-	-	-	-	3.8	2.7	0.8
Lamotrigine	84057-84-1	256.09	15.0	19.2	5.9	-0.7	10.9	-0.7	1.7	1.9
Lidocaine	137-58-6	234.343	13.8	-	7.8	-5.3	10.8	-0.6	1.1	2.6
Melamine	108-78-1	126.123	15.7	16.9	9.6	2.8	12.6	-2.8	-2.5	-2.0
Metformin	657-24-9	129.167	19.2	-	12.3	10.3	-	-5.7	-5.7	-5.4
Metoprolol	51384-51-1	267.369	14.1	-	9.7	-3.2	11.9	-1.5	-1.3	0.1
Sulfamethoxazole	723-46-6	253.28	6.2	-	2.0	0.3	4.1	0.8	0.6	-0.1
Valsartan Acid	164265-78-5	266.26	4.0	5.9	-1.4	-3.7	1.3	3.1	0.9	-1.7

Tab. SI 4: Composition of the synthetic wastewater used as feed for the experiments of varying current densities and varying pH_{feed}. TRIS was added as a buffer to stabilize pH. For the experiment with varying feed pH the pH was stabilized using acid dosing.

Ingredient	Manufacturer	Feed Concentration in M	added into 4L MilliQ: Varying Current Density	added into 4L MilliQ: Varying feed pH: Synthetic Feed
NaCl	VWR	0.05	10.55 g	11.25 g
$Na_2HPO_4*7{\cdot}H_2O$	Merck	0.002	-	1.075 g
$NaH_2PO_4*H_2O$	Merck	0.002	3.12 g	-
TRIS	Merck	0.01	40 mL	-

Tab. SI 5: Overview of operational parameters during investigation of pH dependent transport in ED. All values obtained with DataView-Data Logger and aggregated for the duration of the experiment.

	EC_{Conc} ***in mS/cm***	**$EC_{Diluate}$** ***in mS/cm***	**$pH_{Diluate}$**	**$pH_{Concentrate}$**	**Current** ***in A***	**Current Density** ***in A/m²***	**Voltage** ***in V***
Experiment pH Feed: 7							
Run #1	7.00 ± 0.93	4.32 ± 0.88	6.99 ± 0.00	7.03 ± 0.00	0.19 ± 0.05	1.46 ± 0.38	4.09 ± 1.17
Run #2	7.80 ± 1.15	4.52 ± 1.10	7.49 ± 0.02	7.54 ± 0.00	0.17 ± 0.07	1.36 ± 0.53	3.49 ± 1.41
Experiment pH Feed: 8							
Run #1	7.24 ± 0.86	4.22 ± 0.82	7.96 ± 0.02	8.00 ± 0.03	0.19 ± 0.03	1.51 ± 0.27	4.45 ± 0.91
Run #2	8.24 ± 1.04	4.07 ± 0.97	8.25 ± 0.08	8.34 ± 0.09	0.20 ± 0.00	1.56 ± 0.04	4.10 ± 0.29
Experiment pH Feed: 6							
Run #1	7.74 ± 0.75	3.81 ± 0.70	6.07 ± 0.01	6.03 ± 0.01	0.20 ± 0.00	1.57 ± 0.00	4.82 ± 0.40
Run #2	7.49 ± 1.05	4.63 ± 1.04	6.54 ± 0.03	6.59 ± 0.02	0.17 ± 0.07	1.31 ± 0.58	3.33 ± 1.52
Experiment pH Feed: 4							
Run #1	8.06 ± 1.00	3.70 ± 0.90	3.88 ± 0.04	4.34 ± 0.11	0.18 ± 0.05	1.44 ± 0.41	4.67 ± 1.47
Run #2	7.98 ± 1.02	4.01 ± 0.95	4.39 ± 0.09	4.88 ± 0.13	0.24 ± 0.01	1.87 ± 0.10	4.55 ± 0.49
Experiment pH Feed: 3							
Run #1	8.07 ± 1.07	4.16 ± 1.02	2.83 ± 0.06	3.45 ± 0.22	0.19 ± 0.04	1.50 ± 0.32	4.72 ± 1.16
Run #2	7.97 ± 1.10	4.42 ± 1.07	2.99 ± 0.06	3.61 ± 0.25	0.18 ± 0.06	1.44 ± 0.44	3.88 ± 1.23

Tab. SI 6: Overview of operational parameters during investigation of current density. All values obtained with DataView-Data Logger and aggregated for the duration of the experiment. $pH_{concentrate}$ was not monitored during this experiment

	EC_{Conc} ***in mS/cm***	**$EC_{Diluate}$** ***in mS/cm***	**$pH_{Diluate}$**	**Current** ***in A***	**Current Density** ***in A/m²***	**Voltage** ***in V***
Current :0.8 A/m²						
Run #1	9.36 ± 0.02	1.00 ± 0.00	8.01 ± 0.05	0.10 ± 0.00	0.79 ± 0.00	5.44 ± 0.17
Run #2	9.75 ± 0.02	1.00 ± 0.00	8.04 ± 0.00	0.10 ± 0.00	0.79 ± 0.00	5.66 ± 0.01
Current: 1.0 A/m²						
Run #1	12.38 ± 0.04	1.00 ± 0.00	8.03 ± 0.01	0.13 ± 0.00	1.02 ± 0.00	9.26 ± 0.08
Run #2	9.96 ± 1.03	1.53 ± 1.05	8.23 ± 0.16	0.13 ± 0.00	1.02 ± 0.00	7.76 ± 1.86
Run #3	10.49 ± 0.03	1.00 ± 0.00	8.03 ± 0.00	0.13 ± 0.00	1.02 ± 0.00	9.21 ± 0.17
Run #4	10.58 ± 0.02	1.00 ± 0.00	8.03 ± 0.00	0.13 ± 0.00	1.02 ± 0.00	9.53 ± 0.04
Current: 0.9 A/m²						
Run #1	10.68 ± 0.03	1.00 ± 0.00	8.04 ± 0.01	0.11 ± 0.00	0.86 ± 0.01	8.76 ± 0.08
Run #2	10.78 ± 0.01	1.00 ± 0.00	8.03 ± 0.00	0.11 ± 0.00	0.87 ± 0.00	9.07 ± 0.02
Run #3	10.85 ± 0.04	1.00 ± 0.00	8.03 ± 0.01	0.11 ± 0.00	0.87 ± 0.00	9.39 ± 0.18
Current: 2.0 A/m²						
Run #1	10.93 ± 0.03	1.00 ± 0.01	7.96 ± 0.07	0.25 ± 0.01	1.95 ± 0.05	20.21 ± 0.87
Run #2	11.02 ± 0.04	1.00 ± 0.00	7.96 ± 0.01	0.25 ± 0.00	1.96 ± 0.00	21.02 ± 0.14
Run #3	11.10 ± 0.04	1.00 ± 0.00	8.00 ± 0.02	0.25 ± 0.00	1.96 ± 0.00	21.54 ± 0.18
Run #4	11.22 ± 0.02	1.00 ± 0.00	8.03 ± 0.04	0.25 ± 0.00	1.96 ± 0.00	22.03 ± 0.09

Tab. SI 7: Recovery of analytes for Sartorius RC25 filters used in this study. Each matrix was spiked with 10µL of 1 ng/µL mixed reference standard and filtered through the RC25

	Recovery in %	
	tap water	**ultrapure water**
4/5-Methylbenzotriazole	116.7(±9.32)	95.2(±2.65)
Acesulfame	104.9(±6.75)	100.9(±2.94)
Benzotriazole	n.d.	n.d.
Carbamazepine	106(±9.07)	99.2(±4.45)
Diclofenac	107.3(±11.3)	98.4(±1.53)
Ibuprofen	106.2(±8.73)	97.3(±2.36)
Lamotrigine	101.3(±9.15)	18.5(±8.26)
Lidocaine	95(±10.08)	3.9(±3.54)
Melamine	97.7(±7.2)	73.7(±6.31)
Metformin	104.5(±6.77)	0.1(±0.11)
Metoprolol	105.6(±8.54)	6.9(±5.51)
Sulfamethoxazole	n.d.	n.d.
Valsartan Acid	103.3(±11.38)	94.9(±9.31)

Tab. SI 8: Recovery of inorganic compounds for Sartorius RC25 filters used in this study. Each matrix was spiked with 10µL of 1 ng/µL mixed reference standard and filtered through the RC25 filter. The filtered spiked matrix was compared against a reference that was spiked and centrifuged (15.000 rpm) for 15min. Recovery experiments were performed in triplicate.

	Recovery in %
	ultrapure water
B	79.9(±5.1)
Na	99.3(±1.63)
Mg	98.6(±1.66)
Al	131.2
K	102.2(±2.03)
Ca	97.9(±1.62)
Cr	97(±5.25)
Mn	100(±0)
Fe	104.4(±3.85)
Co	96.4(±6.3)
Ni	94.4(±4.81)
Cu	98.4(±0)
Zn	100.9(±4.02)
As	97(±5.25)
Mo	90.9(±0)
Cd	89.4(±1.89)
Pb	90.9(±0)

Tab. SI 9: Overview of isotope labelled standards spiked into the samples for the use as internal standard. 10 µL were spiked into every 1 mL of sample volume. The target concentration for all internal standards was 10 µg/L.

Isotopically labelled Standard	**Used for matrix correction of ...**
Benzotriazole-d4	Benzotriazole
Metformin-d6	Metformin
5-Methylbenzotriazole-d6	4/5-Methylbenzotriazole
Lidocaine-d10	Lidocaine
Carbamazepine-d10	Carbamazepine
Lamotrigine-13C-15N	Lamotrigine
Valsartan Acid-d4	Valsartan Acid
Metoprolol Acid-d5	Candesartan
Acesulfame-d4	Acesulfame
Ibuprofen-d3	Ibuprofen
Diclofenac-d4	Diclofenac

Tab. SI 10: Overview on matrix effects during LCMS analysis. Matrix effects were determined by with the slopes of the concentration-response functions determined in ultrapure water compared to spiked concentrate, diluate and feed samples. When this comparison yielded non-interpretable results (i.e. negative matrix effects) the matrix effects were estimated based on the area of the associated isotopically labelled internal standard in ultrapure water compared to spiked concentrate, diluate and feed samples.

	Matrix Effects in %		
	Concentrate	**Diluate**	**Initial Feed**
Metformin	-23.5	12.5*	-19.5
Metoprolol	-1*	-5.5*	-2.5
Acesulfame	-6.5	-14.5*	-3.5
Carbamazepine	-4.5*	-10*	-9.5*
Benzotriazole	-9.5*	-5*	-10
Sulfamethoxazole	-5	-13	-22.5
Valsartan Acid	-6*	-14*	NA
Lidocaine	-8*	-13*	-8.5*
Lamotrigine	-13.5*	-36	-31
Diclofenac	-17	-24.5	-24
Ibuprofen	-24.5	-20	-45
Candesartan	-20.5*	-28.5*	NA
4/5-Methylbenzotriazole	-40	-49.5	-65
Melamine	-82	-62.5	-69

Tab. SI 11: Gradient of liquid chromatographic separation method.

	Portion in %		
Time in min	**A (H20)**	**B (MeOH)**	**Flow Rate in mL/min**
0.0	90	10	0.3
0.8	90	10	0.3
7.5	45	55	0.3
21.0	5	95	0.3
28.0	5	95	0.3
29.1	90	10	0.3
31.0	90	10	0.3

Tab. SI 12: MS-Parameters for all analytes, including isotopically-labelled internal standards.

	ESI-Mode	Q1 in u	Q2 in u	RT in min	DP in V	EP in V	CE in eV	CXP in V
Benzotriazole	+	120.01	65.0	7.54	126	10	29	10
		120.01	91.9	7.54	126	10	23	12
Benzotriazole-d4	+	124.01	68.0	7.45	51	10	29	10
		124.01	69.1	7.45	51	10	33	12
Melamine	+	127.01	85.3	0.84	71	10	23	8
		127.01	67.8	0.84	71	10	37	8
Metformin	+	130.06	59.9	0.92	66	10	17	6
		130.06	70.9	0.92	66	10	29	14
Melamine-13C-15N	+	133.06	89.0	0.82	31	10	25	10
		133.06	72.0	0.82	31	10	39	8
4/5-Methylbenzotriazole	+	134.10	77.0	8.90	71	10	31	6
		134.10	78.9	8.90	71	10	29	10
5-Methylbenzotriazole-d6	+	140.06	80.9	8.90	141	10	35	12
		140.10	84.9	8.90	71	10	29	10
Lidocaine	+	235.10	86.1	5.36	76	10	25	8
		235.10	57.9	5.36	76	10	47	8
Carbamazepine	+	237.04	194.1	10.90	106	10	25	6
		237.04	193.1	10.90	106	10	47	8
Lidocaine-d10	+	245.12	96.1	5.29	76	10	25	12
		245.12	64.1	5.29	76	10	57	6
Carbamazepine-d10	+	247.02	204.1	10.77	29	10	29	10
		247.02	202.0	10.77	56	10	47	10
Sulfamethoxazole	+	253.95	92.0	7.55	66	10	37	12
		253.95	155.8	7.55	66	10	21	16

	ESI-Mode	Q1 in u	Q2 in u	RT in min	DP in V	EP in V	CE in eV	CXP in V
Lamotrigine	+	255.99	211.0	6.38	91	10	39	4
		255.99	109.0	6.38	91	10	63	6
Valsartan Acid	+	267.00	151.0	11.08	71	10	55	18
		267.00	206.0	11.08	71	10	25	20
Metoprolol Acid	+	268.07	145.1	5.27	106	10	35	12
		268.07	226.1	5.27	106	10	23	28
Metoprolol	+	268.12	116.1	6.29	81	10	25	6
		268.12	191.1	6.29	81	10	25	4
Metoprolol Acid-d5	+	273.10	196.0	5.21	26	10	27	10
		273.10	150.1	5.21	26	10	35	16
Acesulfame	-	161.90	81.9	4.92	-50	-10	-20	-13
		161.90	77.9	4.92	-50	-10	-40	-13
Acesulfame-d4	-	165.87	86.1	4.87	-25	-10	-20	-7
		165.87	78.0	4.87	-25	-10	-46	-3
Ibuprofen	-	205.08	161.1	17.78	-80	-10	-10	-13
		205.08	159.1	17.78	-80	-10	-10	-13
Ibuprofen-d3	-	208.04	164.1	17.73	-50	-10	-10	-11
		208.04	161.1	17.73	-50	-10	-10	-15
Diclofenac	-	294.00	250.0	17.41	-40	-10	-16	-13
		295.88	252.0	17.41	-40	-10	-16	-11
Diclofenac-d4	-	297.88	254.1	17.34	-50	-10	-18	-13
		298.85	255.0	17.34	-45	-10	-20	-13

Figures

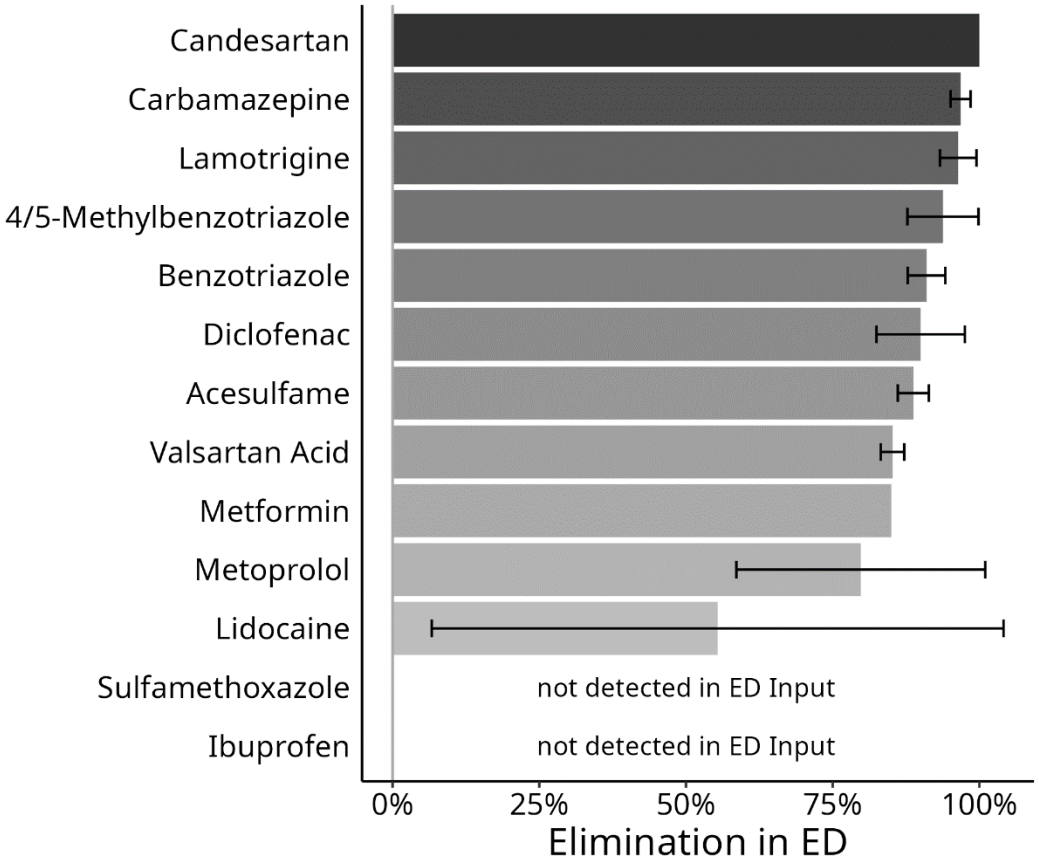

Fig. SI 1: Elimination of micropollutants during nutrient recovery from nitrified wastewater. Data is based on unpublished research. Experiments for nutrient recovery spanned several months.

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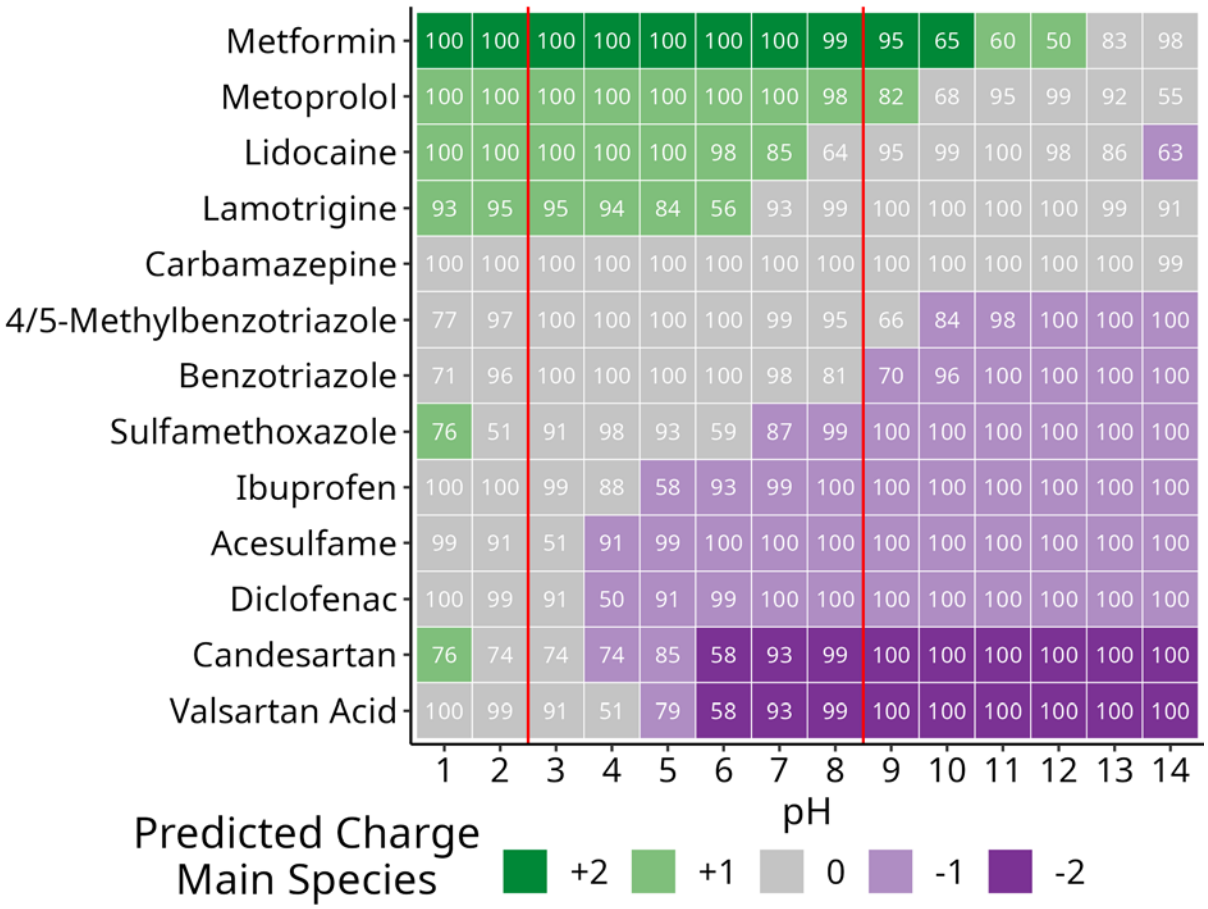

Fig. SI 2: Predicted charge of major species of compounds from pH = 1 to pH = 14 as predicted by ChemAxon. Red lines indicate the pH range under investigation in this study. Numbers represent percentages of the major microspecies present at the corresponding pH.

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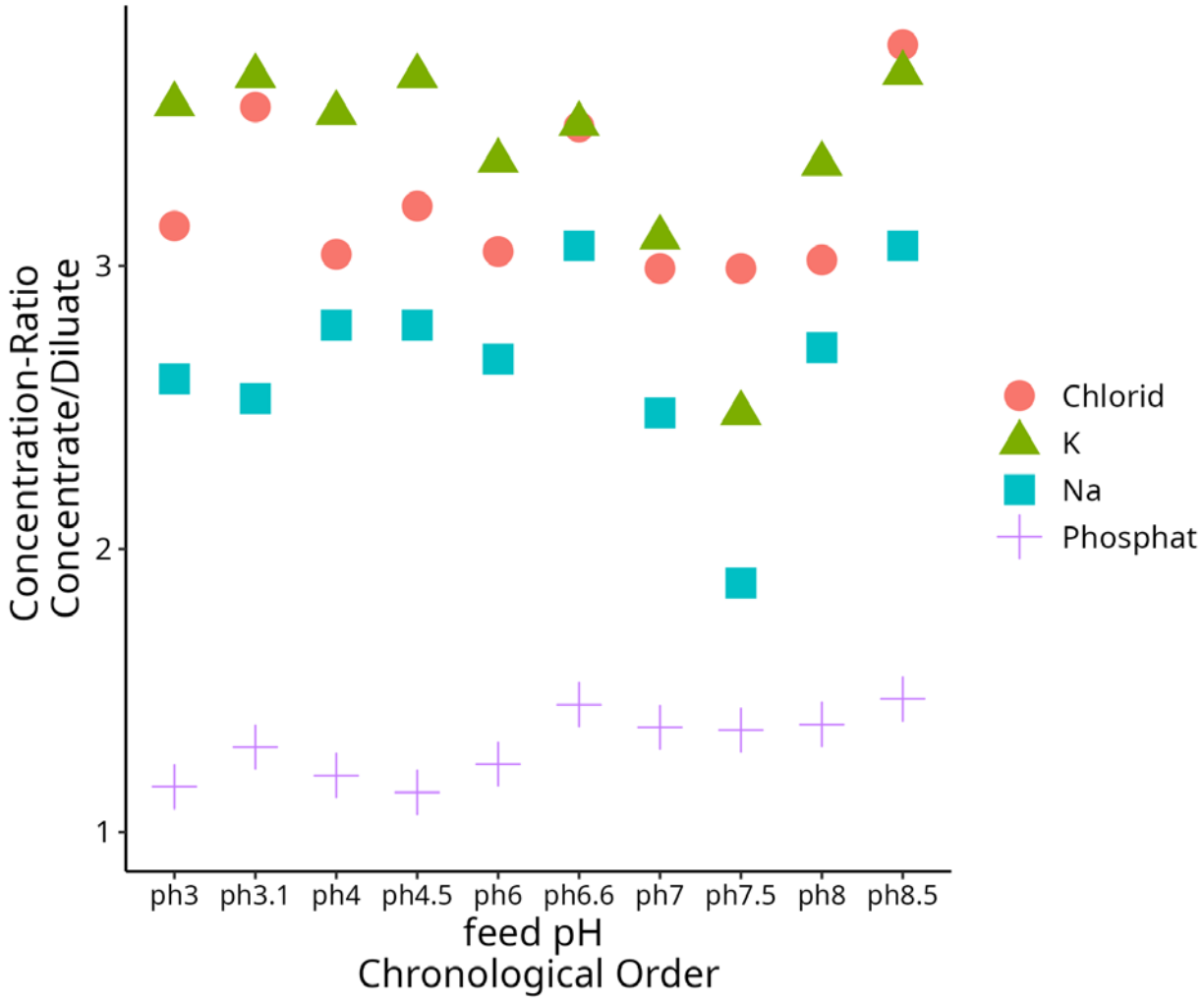

Fig. SI 3: Comparison of Concentrate/Diluate concentration ratios of inorganic reference ions for calculation of TE and phosphate during treatment of synthetic centrate (n = 10) at varying feed pH.

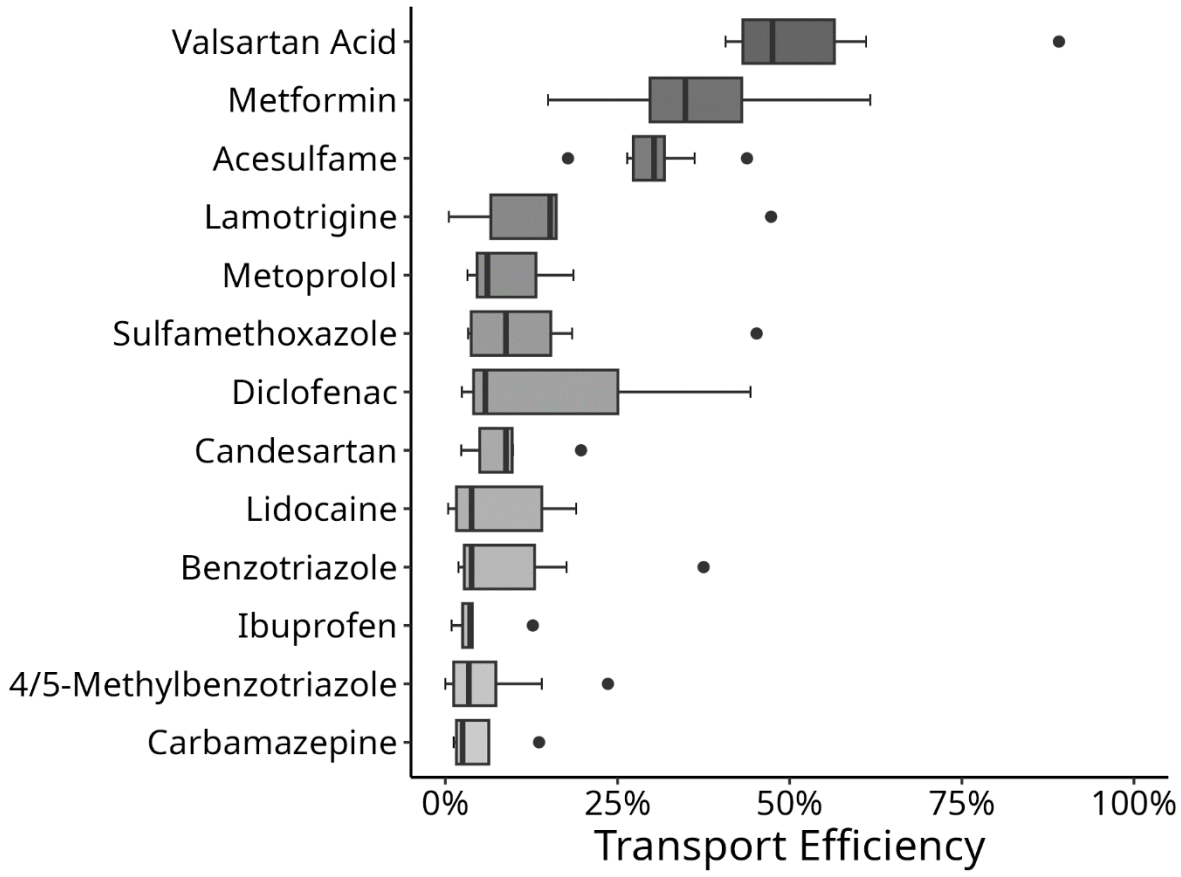

Fig. SI 4: Calculated Transport efficiency (TE) of micropollutants for electrodialysis treatment of synthetic centrate (n = 10). The feed pH was adjusted to pH_{feed}-levels: 8, 7, 6, 4, 3.

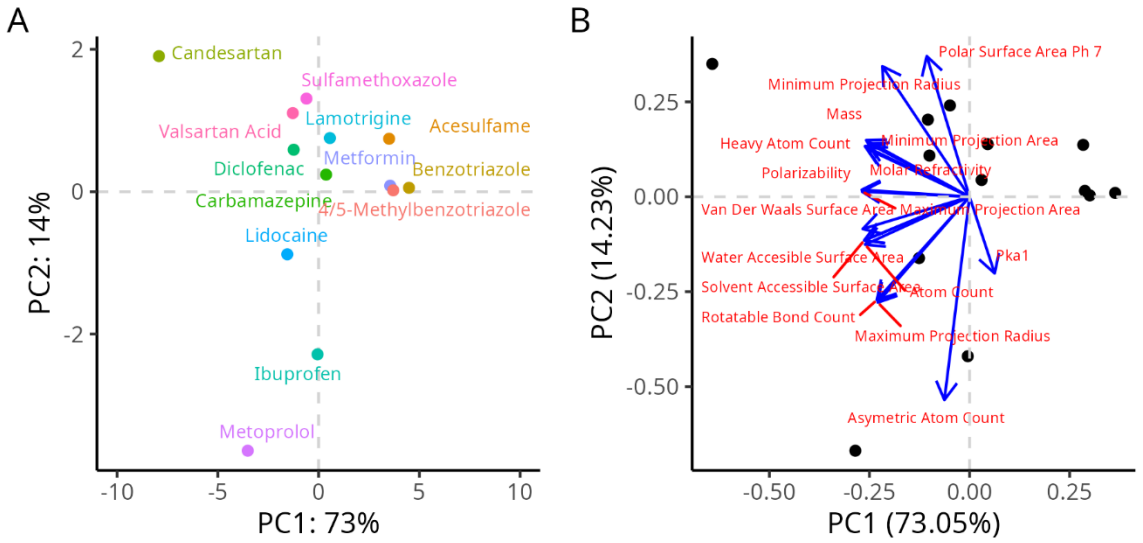

Fig. SI 5: A) PCA across selected physical-chemical properties. B) Loadings of the principal components (blue) and corresponding physical chemical properties (red)

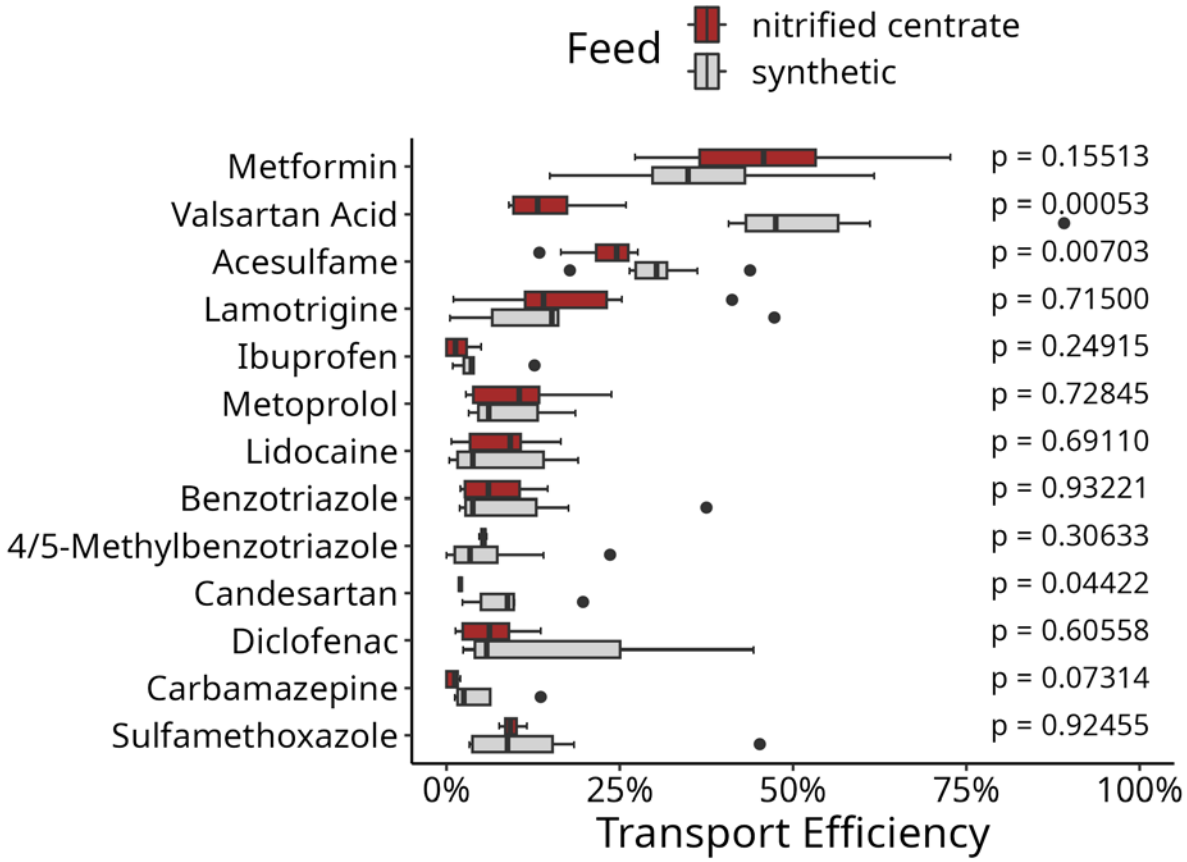

Fig. SI 6: Comparison of transport efficiency (TE) of micropollutants for treatment of synthetic wastewater and real nitrified centrate (n = 10). P-values for a pairwise t-test between TE with synthetic and centrate feed are provided. Both experiments included varying feed pH levels from pH = 8 to pH = 3.

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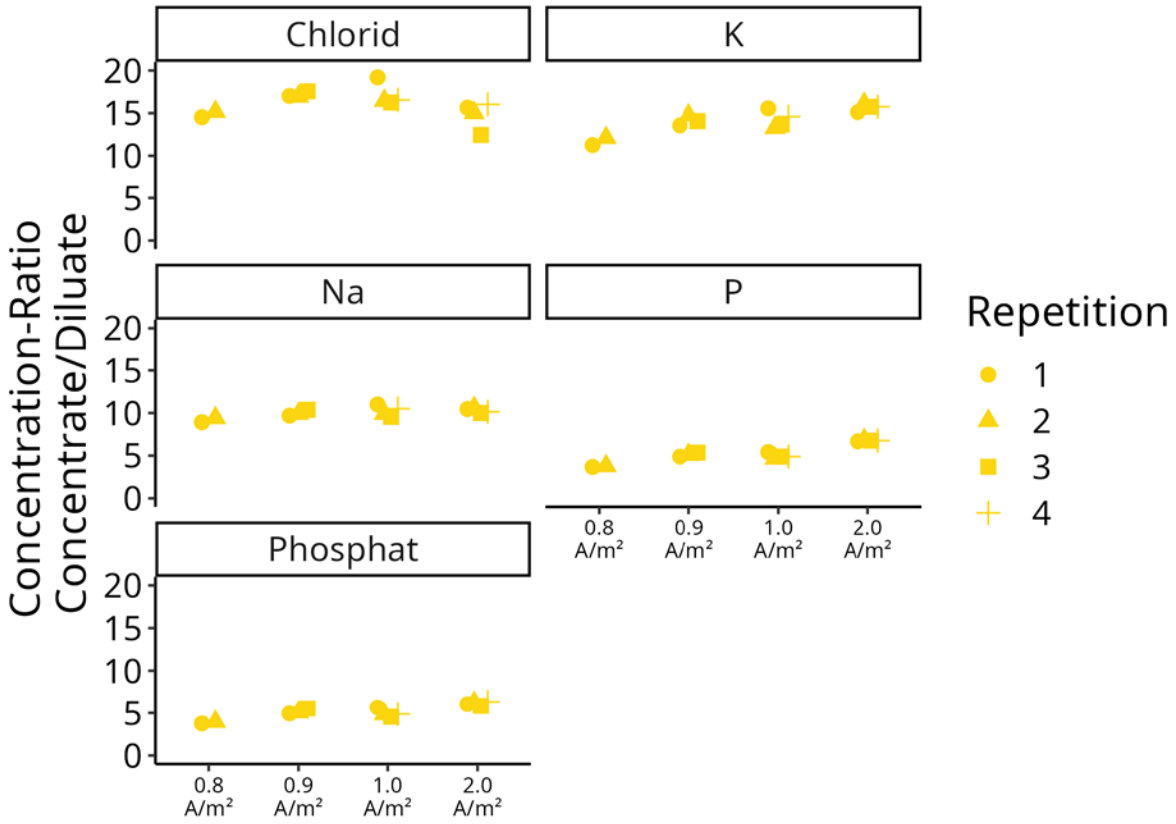

Fig. SI 7: Comparison of Concentrate/Diluate concentration ratios of inorganic reference ions for calculation of TE and phosphate as well as P_{total} during treatment of synthetic centrate at varying feed current densities. While the experiments at 0.8, 0.9 and 1.0 A/m² were performed below the limiting current density. The experiment at 2.0 A/m² was performed at overlimiting current density.

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