

## **SUPPLEMENTARY MATERIAL**

### **Integration of a 3D-printed electrochemical reactor with a tubular membrane photoreactor to promote sulfate-base advanced oxidation processes**

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**Table SM-1** Experimental data (SERPIC-UCLM<sup>®</sup> cell) vs. literature data of distinct electrochemical systems regarding mass transport correlation  $k_m A = q v_{avg}^b$ .

Electrochemical system	$v_{avg}$ ( $\times 10^{-2}$ m s <sup>-1</sup> )	$k_m A = q v_{avg}^b$	References
Customized reactors	0.5 – 10	$k_m A = 1.26 v_{avg}^{0.48}$	[1] <sup>a</sup>
	0.5 – 10	$k_m A = 0.61 v_{avg}^{0.45}$	[1] <sup>b</sup>
	0.5 – 10	$k_m A = 0.43 v_{avg}^{0.47}$	[1] <sup>c</sup>
	1 – 17 <sup>d</sup>	$k_m A = 0.000309 v_{avg}^{0.386}$	[2] <sup>e</sup>
	1 – 17 <sup>d</sup>	$k_m A = 0.00067 v_{avg}^{0.526}$	[2] <sup>f</sup>
	1 – 9 <sup>d</sup>	$k_m A = 0.00224 v_{avg}^{0.492}$	[2] <sup>g</sup>
	1 – 16	$k_m A = 0.00236 v_{avg}^{0.58}$	[3] <sup>h</sup>
	1 – 16	$k_m A = 0.0828 v_{avg}^{0.82}$	[3] <sup>i</sup>
	1 – 16	$k_m A = 0.119 v_{avg}^{0.53}$	[3] <sup>j</sup>
MicroFlow Cell	1.3 – 23	$k_m A = (2.29 \pm 0.07) \times 10^{-2} v_{avg}^{(0.58 \pm 0.02)}$	[4]
e <sup>-</sup> NETmix	10 – 180	$k_m A = (3.99 \pm 0.04) \times 10^{-1} v_{avg}^{(0.43 \pm 0.02)}$	[4]
SERPIC-UCLM <sup>®</sup> cell	1.1 – 7.8	$k_m A = (0.0422 \pm 0.0005) v_{avg}^{0.500 \pm 0.003}$	This work

<sup>a</sup> with Ni foam electrode G100;

<sup>b</sup> with Ni foam electrode G60;

<sup>c</sup> with Ni foam electrode G45;

<sup>d</sup> Data taken from the plot;

<sup>e</sup> With Pt/Ti plate 2D electrode;

<sup>f</sup> With Pt/Ti plate electrode with TP;

<sup>g</sup> With Pt/Ti mesh electrode;

<sup>h</sup> With porous Pt-Ir/Ti plate electrode with TP;

<sup>i</sup> With porous 3D Pt-Ir/Ti fine mesh electrode;

<sup>j</sup> With porous 3D Pt-Ir/Ti felt electrode.

**Table SM-2** Experimental data (SERPIC-UCLM<sup>®</sup> cell) vs. literature data of distinct electrochemical systems regarding mass transport correlation  $Sh = a Re^b Sc^c Le^d$ .

Electrochemical system	$Re$	$Sh = a Re^b Sc^c Le^d$	References
Customized reactors	148 – 6109	$Sh = 0.28 Re^{0.70} Sc^{0.33}$	[5] <sup>a</sup>
	< 2380	$Sh = 28.4 Re^{0.23} Sc^{0.33} Le^{0.33}$	[6] <sup>b</sup>
	93 – 371	$Sh = 1.88 Re^{0.61} Sc^{1/3}$	[7] <sup>c</sup>
	93 – 371	$Sh = 1.11 Re^{0.78} Sc^{1/3}$	[7] <sup>d</sup>
	93 – 371	$Sh = 1.74 Re^{0.68} Sc^{1/3}$	[7] <sup>e</sup>
FM01-LC reactor	200 – 1000	$Sh = 0.74 Re^{0.62} Sc^{1/3}$	[8] <sup>f</sup>
	187 – 1407	$Sh = 0.617 Re^{0.489} Sc^{0.33}$	[9] <sup>g</sup>
	500 – 2200	$Sh = 0.18 Re^{0.73} Sc^{1/3}$	[10] <sup>h</sup>
DiaCell <sup>®</sup> reactor	100 – 2500	$Sh = 0.141 Re^{0.70} Sc^{0.33}$	[11] <sup>i</sup>
MicroFlow Cell	100 – 1750	$Sh = (0.45 \pm 0.03) Re^{(0.543 \pm 0.008)} Sc^{1/3}$	[4]
$e^-$ NETmix	100 – 1750	$Sh = (1.3 \pm 0.1) Re^{(0.43 \pm 0.02)} Sc^{1/3}$	[4]
SERPIC – UCLM <sup>®</sup> cell	110 – 790	$Sh = (2.593 \pm 0.060) Re^{(0.500 \pm 0.004)} Sc^{1/3}$	This work

<sup>a</sup> Parallel plate reactor with Pt/Ti cathode, Ni anode, and without TP;

<sup>b</sup> Rectangular flow cell with nanostructured Ni electrodeposited on a SS plate and without TP;

<sup>c</sup> 3D-printed Filter-Press electrochemical reactor with Ni electrodes and a diamond-shaped 3D-printed TP;

<sup>d</sup> 3D-printed Filter-Press electrochemical reactor with Ni foam electrodes;

<sup>e</sup> 3D-printed Filter-Press electrochemical reactor with square-shaped 3D-printed TP;

<sup>f</sup> With Ni electrodes and TP;

<sup>g</sup> With 316 SS plate electrodes;

<sup>h</sup> With Ni electrodes and without TP;

<sup>i</sup> With BDD as anode and SS as cathode.

**Table SM-3.** Identification and characteristics of the target CECs and respective limits of quantification in RO<sub>c</sub> and NF<sub>c</sub>.

Category	Pollutant	Acronym	Chemical composition	Molecular weight (g mol <sup>-1</sup> )	LQ <sub>ROc</sub> <sup>a</sup> (µg L <sup>-1</sup> )	LQ <sub>NFc</sub> <sup>a</sup> (µg L <sup>-1</sup> )
Angiotensin II Receptor Blockers	Valsartan	VSTN	C <sub>24</sub> H <sub>29</sub> N <sub>5</sub> O <sub>3</sub>	435.52	0.17	0.17
	Irbesartan	ISTN	C <sub>25</sub> H <sub>28</sub> N <sub>6</sub> O	428.53	0.14	0.30
	Losartan	LSTN	C <sub>22</sub> H <sub>23</sub> ClN <sub>6</sub> O	422.91	0.37	1.00
Beta-blocking agents	Atenolol	ATNL	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>	266.34	0.12	0.18
	Bisoprolol	BSPL	C <sub>18</sub> H <sub>31</sub> NO <sub>4</sub>	325.44	0.05	0.22
Carbamazepine and Metabolites	Carbamazepine	CBZ	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	236.27	0.06	0.05
	10,11 Carbamazepine-epoxide	CBZ-EPX	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	252.27	0.12	0.10
Fire Retardants	Melamine	MLN	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub>	126.12	1.15	1.00
Herbicides	Diuron	DRN	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	233.1	0.06	0.08
Insect Repellents	N,N-diethyl-meta-toluamide	DEET	C <sub>12</sub> H <sub>17</sub> NO	191.27	0.04	0.05
Anti-Inflammatory Drugs	Diclofenac	DCF	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>2</sub>	318.13	0.51	0.40
Non-ionic X-ray contrast agent	Iopromide	IOP	C <sub>18</sub> H <sub>24</sub> I <sub>3</sub> N <sub>3</sub> O <sub>8</sub>	791.11	1.06	1.00
Antibiotic	Sulfamethoxazole	SMX	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	253.28	0.08	0.10
Antidepressant	Venlafaxine	VLX	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub>	277.40	0.07	0.20

<sup>a</sup> Limit of quantification for reverse osmosis concentrate (LQ<sub>ROc</sub>) and for nanofiltration concentrate (LQ<sub>NFc</sub>) determined according to the methodology described in Rodrigues-Silva et al. [12].

**Table SM-4.** Physicochemical characteristics and native concentrations of target CECs in the feed water for RO and NF membrane system.

Parameters	Units	Influent	
		RO	NF
pH	-	7.2	7.3
Conductivity	$\mu\text{S cm}^{-1}$	1387	1079
Chemical Oxygen Demand (COD)	$\text{mg L}^{-1}$	120	70
Dissolved Organic Carbon (DOC)	$\text{mg L}^{-1}$	16.2	13.1
Dissolved Inorganic Carbon (DIC)	$\text{mg L}^{-1}$	61.5	50.0
Total Suspended Solids (TSS)	$\text{mg L}^{-1}$	64.5	31.5
Chloride ( $\text{Cl}^-$ )	$\text{mg L}^{-1}$	132	159
Nitrate ( $\text{NO}_3^-$ )	$\text{mg L}^{-1}$	5.1	5.8
Nitrite ( $\text{NO}_2^-$ )	$\text{mg L}^{-1}$	13.8	8.1
Sulfate ( $\text{SO}_4^{2-}$ )	$\text{mg L}^{-1}$	58	57
Phosphate ( $\text{PO}_4^{3-}$ )	$\text{mg L}^{-1}$	14.4	10.6
Ammonium ( $\text{NH}_4^+$ )	$\text{mg L}^{-1}$	43.6	27.4
Potassium ( $\text{K}^+$ )	$\text{mg L}^{-1}$	24.1	25.4
Sodium ( $\text{Na}^+$ )	$\text{mg L}^{-1}$	109	124
Calcium ( $\text{Ca}^{2+}$ )	$\text{mg L}^{-1}$	32.7	28.5
Magnesium ( $\text{Mg}^{2+}$ )	$\text{mg L}^{-1}$	7.0	5.2
Atenolol (ATNL)	$\mu\text{g L}^{-1}$	<0.12	<0.18
Bisoprolol (BSPL)	$\mu\text{g L}^{-1}$	0.3	0.6
Carbamazepine (CBZ)	$\mu\text{g L}^{-1}$	0.5	0.9
CBZ 10,11-epoxide (CBZ-EPX)	$\mu\text{g L}^{-1}$	<0.12	0.5
DEET (DEET)	$\mu\text{g L}^{-1}$	0.6	<0.05
Diclofenac (DCF)	$\mu\text{g L}^{-1}$	0.7	1.8
Diuron (DRN)	$\mu\text{g L}^{-1}$	<0.06	0.2
Iopromide (IOP)	$\mu\text{g L}^{-1}$	4.6	3.8
Irbesartan (ISTN)	$\mu\text{g L}^{-1}$	1.0	2.0
Losartan (LSTN)	$\mu\text{g L}^{-1}$	0.4	<1.0
Melamine (MLN)	$\mu\text{g L}^{-1}$	1.8	3.0
Sulfamethoxazole (SMX)	$\mu\text{g L}^{-1}$	0.4	0.3
Valsartan (VSTN)	$\mu\text{g L}^{-1}$	1.1	<0.17
Venlafaxine (VLX)	$\mu\text{g L}^{-1}$	0.3	0.8

**Table SM-5.** Molar extinction coefficient, quantum yield and rate constants for reaction with HO• and SO<sub>4</sub><sup>•-</sup> of each target CECs.

CECs	$\epsilon_{254}^a$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\Phi_{254}^a$ (mol Ein <sup>-1</sup> )	$k_{\text{SO}_4^{\bullet-}b}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{\text{HO}^{\bullet-c}}$ (M <sup>-1</sup> s <sup>-1</sup> )
VSTN	$2.1 \times 10^3$	Unknown	Unknown	$1.0 \times 10^{10}$
ISTN	$1.5 \times 10^4$	Unknown	$1.2 \times 10^8$	$1.9 \times 10^8$
LSTN	$1.2 \times 10^4$	$1.5 \times 10^{-2}$	Unknown	Unknown
ATNL	$3.5 \times 10^2$	$6.5 \times 10^{-2}$	$1.3 \times 10^{10}$	$7.1 \times 10^{10}$
BSPL	Unknown	Unknown	Unknown	Unknown
CBZ	$5.8 \times 10^3$	$3.3 \times 10^{-3}$	$1.92 \times 10^9$	$8.8 \times 10^9$
CBZ-EPX	Unknown	Unknown	Unknown	Unknown
MLN	Unknown	Unknown	$1.0 \times 10^5$	$1.0 \times 10^4$
DRN	$1.6 \times 10^4$	$1.4 \times 10^{-2}$	$5.2 \times 10^9$	$5.0 \times 10^9$
DEET	$0.9 \times 10^3$	$1.0 \times 10^{-2}$	$(1.9 - 0.1) \times 10^9$	$5.0 \times 10^9$
DCF	$6.8 \times 10^3$	$2.3 \times 10^{-1}$	$6.7 \times 10^9$	$7.5 \times 10^9$
IOP	$2.2 \times 10^4$	$3.9 \times 10^{-2}$	$(1-2) \times 10^4$	$3.3 \times 10^9$
SMX	$1.3 \times 10^4$	$8.4 \times 10^{-2}$	$8.8 \times 10^9$	$5.5 \times 10^9$
VLX	$3.8 \times 10^2$	$9.7 \times 10^{-2}$	$3.5 \times 10^9$	$8.6 \times 10^9$

<sup>a</sup> Values for molar extinction coefficient ( $\epsilon_{254\text{nm}}$ ) and quantum yield ( $\Phi_{254\text{nm}}$ ) were obtained from Allard et al. [13]; Mallegowda et al. [14]; Parry & Young. [15]; Rahmadhani et al. [16]; Wols et al. [17]; Wols & Hofman-Caris. [18]; Starling et al. [19].

<sup>b</sup> Kinetic constants for the reaction with SO<sub>4</sub><sup>•-</sup> ( $k_{\text{SO}_4^{\bullet-}}$ ) were obtained from Canle et al. [20]; Chan et al. [21]; Lian et al. [22]; Liu et al. [23]; Mahdi Ahmed et al. [24]; Matta et al. [25]; Maurino et al. [26]; Mutke et al.[27]; Tay et al. [28].

<sup>c</sup> Kinetic constants for the reaction with HO• ( $k_{\text{HO}^{\bullet}}$ ) were obtained from Huber et al. [29]; Lian et al. [22]; Mandal [30]; Maurino et al. [26]; Mutke et al. [27]; Song et al., [31]; Sauter et al. [32].

**Table SM-6.** Statistical differences (*t*-student test) for operational parameters influencing the treatment of RO<sub>C</sub>.

CECs	1.2 mM PMSA vs. 1.2 mM PDS
	<i>p</i> -value
ATNL	0.0199
BSPL	0.0084
CBZ	0.0693
CBZ-EPX	0.0139
DEET	0.2397
DCF	0.1857
DRN	0.0065
IOP	0.1261
ISTN	0.0045
LSTN	0.0110
MLN	0.3735
SMX	0.0272
VSTN	0.8494
VLX	0.0071

**Table SM-7.** Statistical analyses (One-way ANOVA) for operational parameters influencing the treatment of NF<sub>C</sub>.

CECs	Conditions	One-way ANOVA							
		Mean Diff	SEM	<i>q</i> Value	Prob	Alpha	Sig	LCL	UCL
<b>CBZ-EPX</b>	1.2 mM PDS vs. 1.2 mM PMSA	4.09	3.09	1.87	0.43347	0.05	0	-5.39	13.58
	2.4 mM PMSA vs. 1.2 mM PMSA	32.00	3.09	14.64	0.00011	0.05	1	22.51	41.48
<b>SMX</b>	1.2 mM PDS vs. 1.2 mM PMSA	12.06	1.97	8.65	0.00211	0.05	1	6.01	18.11
	2.4 mM PMSA vs. 1.2 mM PMSA	21.76	1.97	15.62	0.00008	0.05	1	15.72	27.82
<b>DCF</b>	1.2 mM PDS vs. 1.2 mM PMSA	1.17	1.16	1.43	0.59818	0.05	0	-2.38	4.71
	2.4 mM PMSA vs. 1.2 mM PMSA	6.15	1.16	7.52	0.00433	0.05	1	2.60	9.69
<b>ISTN</b>	1.2 mM PDS vs. 1.2 mM PMSA	0.53	0.04	17.30	0.00004	0.05	1	0.40	0.67
	2.4 mM PMSA vs. 1.2 mM PMSA	0.48	0.04	15.67	0.00008	0.05	1	0.35	0.62

**Table SM-8.** Statistical analyses (Non-parametric ANOVA) for operational parameters influencing the treatment of NF<sub>C</sub>.

<b>CECs</b>	<b>Conditions</b>	<b>Mean Rank Diff</b>	<b>Z</b>	<b>Prob</b>	<b>Sig</b>
<b>CBZ</b>	1.2 mM PDS vs. 1.2 mM PMSA	3.50	1.56	0.35	0
	2.4 mM PDS vs. 1.2 mM PMSA	-1.00	-0.50	1.00	0
<b>DRN</b>	1.2 mM PDS vs. 1.2 mM PMSA	0.83	0.37	1.00	0
	2.4 mM PDS vs. 1.2 mM PMSA	-3.50	-1.56	0.35	0
<b>LSTN</b>	1.2 mM PDS vs. 1.2 mM PMSA	2.50	1.12	0.79	0
	2.4 mM PDS vs. 1.2 mM PMSA	-2.50	-1.12	0.79	0
<b>IOP</b>	1.2 mM PDS vs. 1.2 mM PMSA	2.33	1.17	0.73	0
	2.4 mM PDS vs. 1.2 mM PMSA	-1.50	-0.67	1.00	0
<b>MLN</b>	1.2 mM PDS vs. 1.2 mM PMSA	0.67	0.33	1.00	0
	2.4 mM PDS vs. 1.2 mM PMSA	3.33	1.63	0.31	0
<b>BSPL</b>	1.2 mM PDS vs. 1.2 mM PMSA	-1.00	-0.45	1.00	0
	2.4 mM PDS vs. 1.2 mM PMSA	-5.00	-2.24	0.01	0
<b>VLX</b>	1.2 mM PDS vs. 1.2 mM PMSA	-1.00	-0.45	1.00	0
	2.4 mM PDS vs. 1.2 mM PMSA	-5.00	-2.24	0.01	0

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