SUPPLEMENTARY INFORMATION

Supramolecular solvents for the valorization of coffee wastewater

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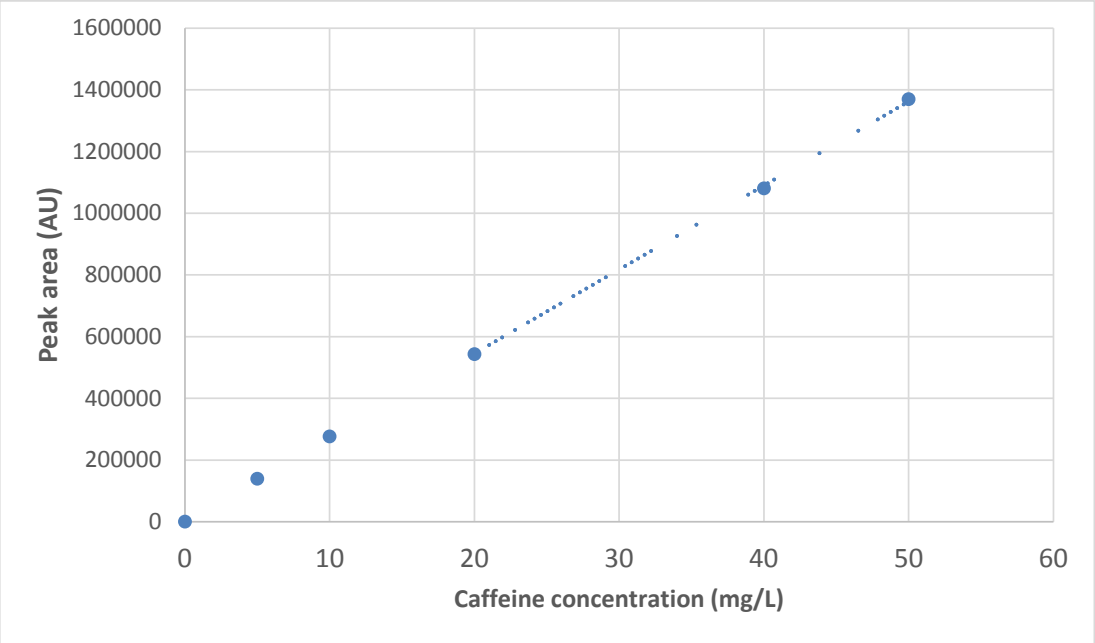
Figure S1. Standard curve for caffeine (LC-UV, 254 nm)



Calibration curve statistics; y= 27,219 +1110: R^2= 0.9998

	Coefficients	*Standard Error*	*Lower 95%*	*Upper 95%*
Intercept	1109.9	3946.1	-9846.3	12066.2
Slope	27219.5	142.1	26824.9	27614.1

Statistics

ANOVA

	df	*SS*	*MS*	*F*	***Significance F***
Regression	1	1.49724E+12	1.49724E+12	36675.4	**4.45988E-09**
Residual	4	163296573.5	40824143.36		
Total	5	1.4974E+12			

df: degrees of freedom; SS: sum of squares; MS: mean squares; F: calculated F for the null hypothesis (linear regression not significant) as MSreg/MSres; Significance F: associated p-value (linear regression significant for Significance F ≤0.05)

Figure S2. LC-UV chromatograms of A) a standard of caffeine (10 mg/L), B) the coffee wastewater (CWW), C) hexanol-SUPRAS extract of CWW, optimal conditions and D) decanoic acid-SUPRAS extract of CWW, optimal conditions. Caffeine peak appearing at 6.5 min. B, C and D were diluted 12 times before injection.

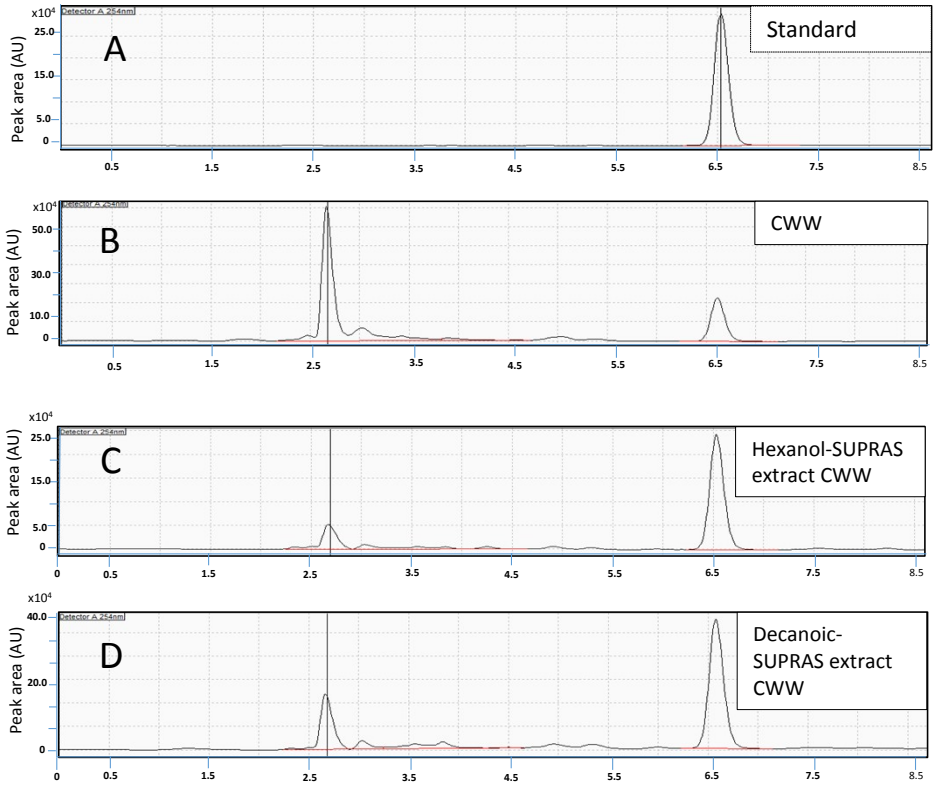


Figure S3. **Extraction of caffeine by SUPRAS from CWW under resting conditions, expressed as mg of recovered caffeine per liter of wastewater against time (3.5-30 min).**

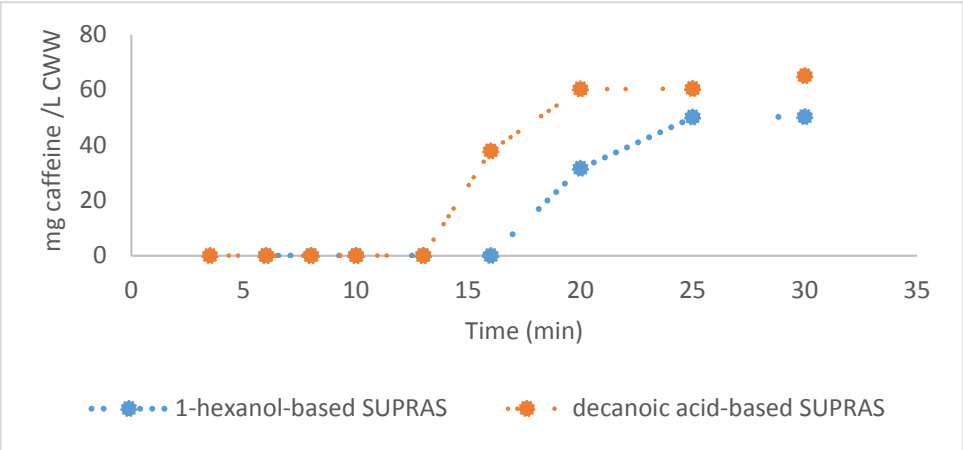


Table S1. **Absorbance values for $ABTS^{\bullet+}$ antioxidant activity (AA) of SUPRAS extracts. AA(%)= Abs_0-Abs_{30}/Abs_0*100, where Abs_0 is the absorbance of $ABTS^{+}$ reagent solution at time zero and Abs_{30} is the absorbance of the reagent in the presence of SUPRAS extracts (previously diluted in 1:10 with methanol) at 30 minutes of reaction.**

	Abs0	Abs30 (hexanol SUPRAS extract)	Abs30 (decanoic acid SUPRAS extract)	AA % (hexanol SUPRAS extract)	AA % (decanoic acid extract)
Replicate 1	0.709	0.321	0.411	54.7	42.03
Replicate 2	0.703	0.353	0.416	50.2	41.33
Replicate 3	0.710	0.320	0.415	54.6	42.00
Average				**53.2**	**41.8**
SD				**2.6**	**0.4**
SDR				**4.8**	**0.9**

Table S2. Degradation kinetics (zero-order, first-order and second-order) of caffeine in 1-hexanol-based SUPRAS at different temperatures. CA: caffeine concentration in SUPRAS extract (mg/L)

T = 4 °C				T = 14 °C				T = 24 °C			
Days	CA	lnCA	1/CA	Days	CA	lnCA	1/CA	Days	CA	lnCA	1/CA
0	122	4.80	0.008	0	122	4.80	0.008	0	122	4.80	0.008
1	112	4.72	0.009	1	103	4.64	0.010	1	110	4.70	0.009
2	115	4.75	0.009	2	117	4.77	0.009	2	117	4.76	0.009
6	105	4.66	0.009	6	104	4.65	0.010	6	105	4.65	0.010
9	108	4.68	0.009	9	99	4.60	0.010	9	106	4.67	0.009
16	112	4.72	0.009	16	115	4.74	0.009	16	116	4.75	0.009
23	106	4.67	0.009	23	107	4.67	0.009	23	104	4.64	0.010
30	109	4.69	0.009	30	115	4.75	0.009	30	112	4.72	0.009
50	113	4.73	0.009	50	116	4.75	0.009	50	109	4.69	0.009
60	113	4.73	0.009	60	113	4.73	0.009	60	111	4.71	0.009

Table S3. Degradation kinetics (zero-order, first-order and second-order) of caffeine in decanoic acid-based SUPRAS at different temperatures. CA: caffeine concentration in SUPRAS extract (mg/L)

T = 4 °C				T = 14 °C				T = 24 °C			
Days	CA	lnCA	1/CA	Days	CA	lnCA	1/CA	Days	CA	lnCA	1/CA
0	196	5.28	0.005	0	196	5.28	0.005	0	196	5.28	0.005
1	184	5.21	0.005	1	190	5.25	0.005	1	179	5.19	0.006
2	180	5.19	0.006	2	176	5.17	0.006	2	185	5.22	0.005
6	172	5.15	0.006	6	176	5.17	0.006	6	172	5.15	0.006
9	170	5.14	0.006	9	160	5.08	0.006	9	170	5.14	0.006
16	187	5.23	0.005	16	181	5.20	0.006	16	185	5.22	0.005
23	167	5.12	0.006	23	170	5.14	0.006	23	170	5.14	0.006
30	170	5.14	0.006	30	188	5.24	0.005	30	181	5.20	0.006
50	186	5.23	0.005	50	188	5.24	0.005	50	175	5.16	0.006
60	185	5.22	0.005	60	180	5.19	0.005	60	178	5.18	0.006

Figure S4. Degradation kinetics of caffeine in 1-hexanol-based SUPRAS. CA: caffeine concentration in SUPRAS extract (mg/L). CA (zero-order plot), lnCA (first-order plot) and 1/CA (second-order plot) are plotted for each temperature against time (0-60 days).

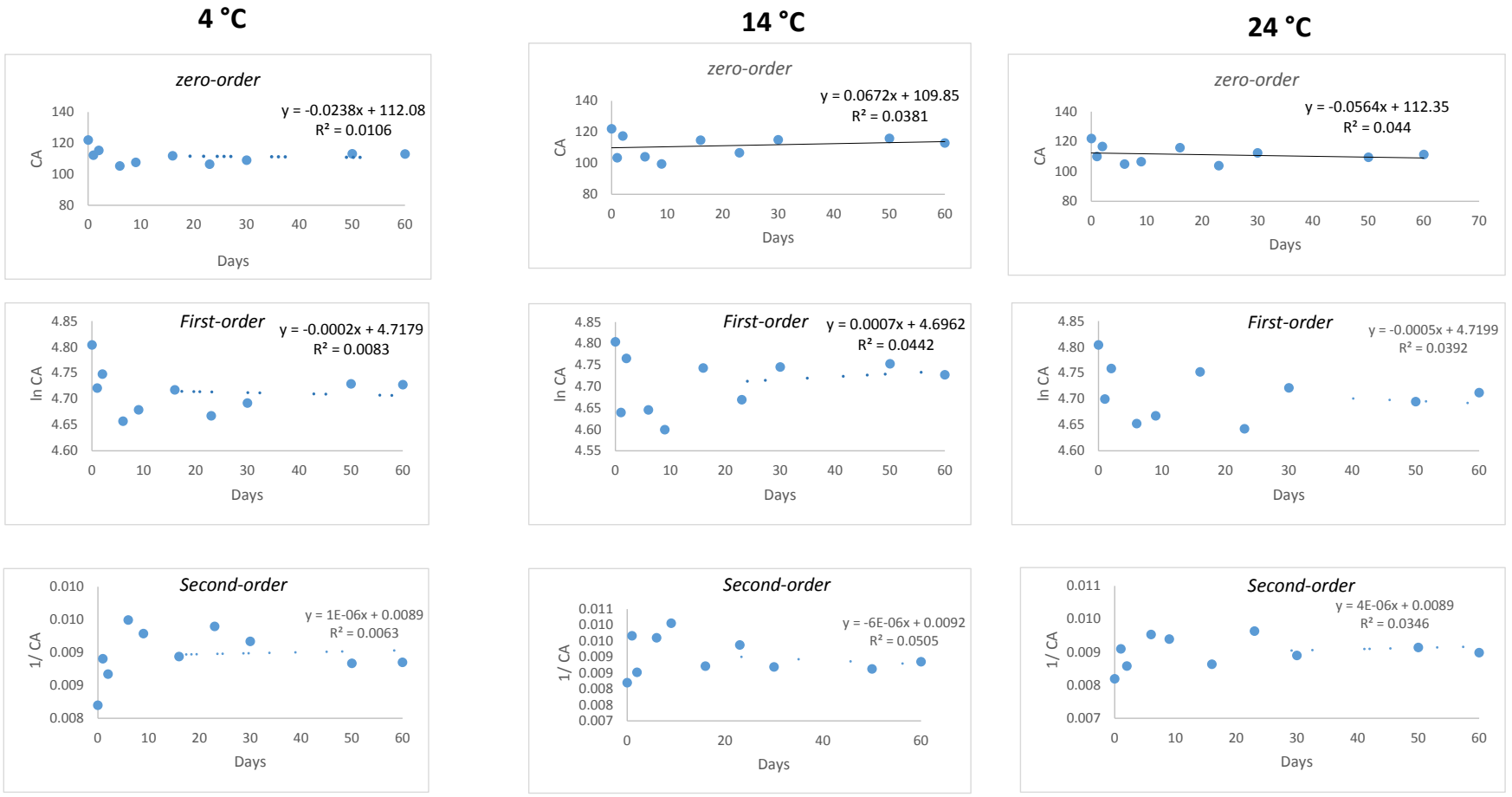


Figure S5. Degradation kinetics of caffeine in decanoic acid-based SUPRAS. CA: caffeine concentration in SUPRAS extract (mg/L). CA (zero-order plot), lnCA (first-order plot) and 1/CA (second-order plot) are plotted for each temperature against time (0-60 days).

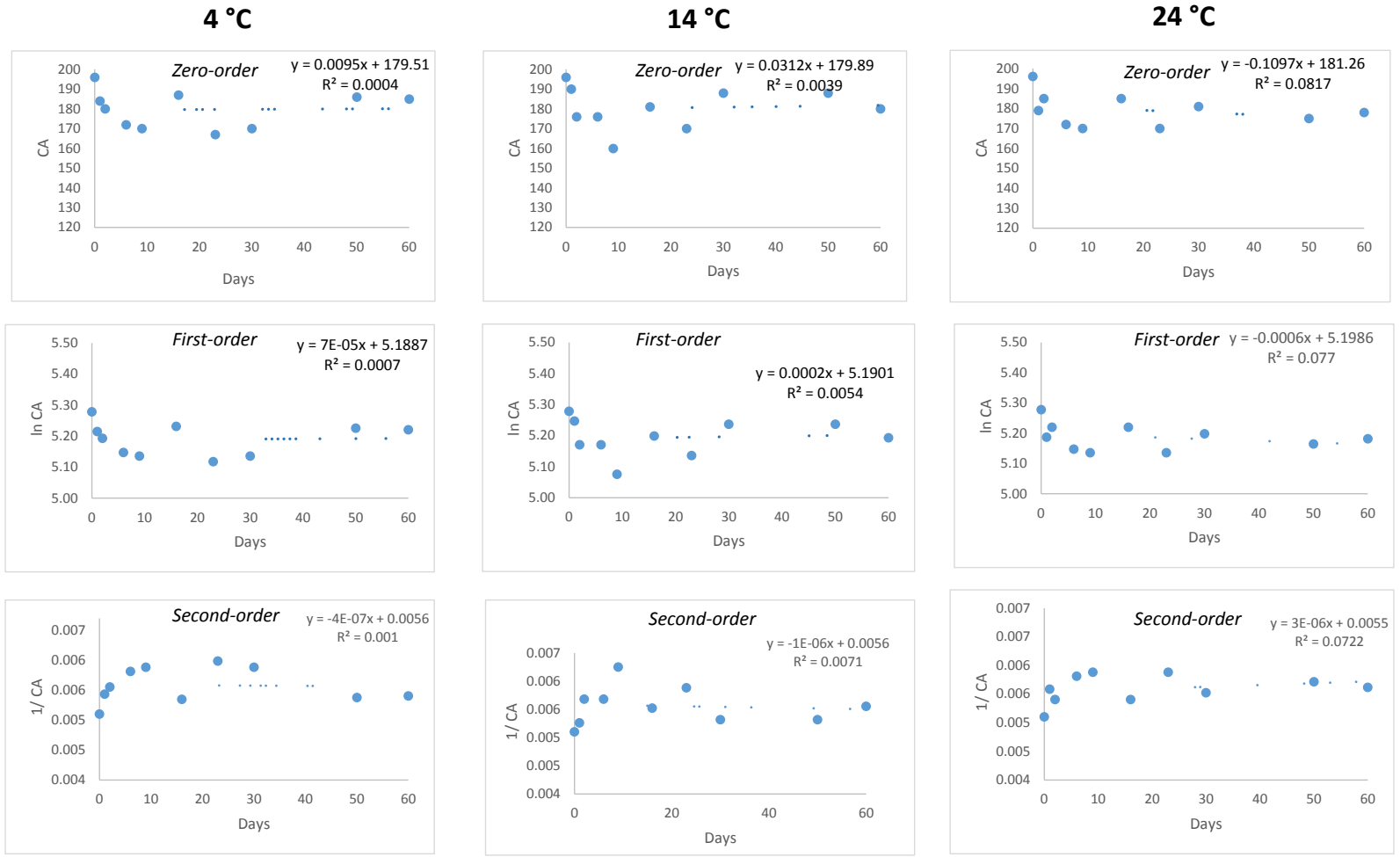


Table S4. ANOVA (two factors) for caffeine content in 1-hexanol-based SUPRAS. Time: 0-60 days, temperature: 4, 14 and 24 °C

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Time	2182.895	9	242.543	12.289	5.21806E-06	2.456
Temperature	2.911	2	1.455	0.073	**0.929**	3.554
Error	355.236	18	19.735			
	2541.043	29				
Total	2182.895	9	242.543	12.289	5.21806E-06	2.456

SS: sum of squares; df: degrees of freedom; MS: mean squares; F: calculated F for the null hypothesis (not significance) as MSreg/MSres; Significance F: associated p-value (Significance F ≤0.05)

Table S5. ANOVA (two factors) for caffeine content in decanoic acid-based SUPRAS. Time: 0-60 days, temperature: 4, 14 and 24 °C

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Time	1939.367	9	215.485	8.044	0.0001	2.456
Temperature	9.866	2	4.933	0.184	**0.833**	3.554
Error	482.133	18	26.785			
Total	2431.367	29				

SS: sum of squares; df: degrees of freedom; MS: mean squares; F: calculated F for the null hypothesis (not significance) as MSreg/MSres; Significance F: associated p-value (Significance F ≤0.05)