Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Enhanced Extraction of Caffeine from Guaraná Seeds using Aqueous Solutions of Ionic Liquids

Ana Filipa M. Cláudio,[a] Ana M. Ferreira,[a] Mara G. Freire*[a] and João A. P. Coutinho*[a]

[a]Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

*Corresponding author

Tel: +351 234370200; Fax: +351 234370084; E-mail address: maragfreire@ua.pt; jcoutinho@ua.pt.

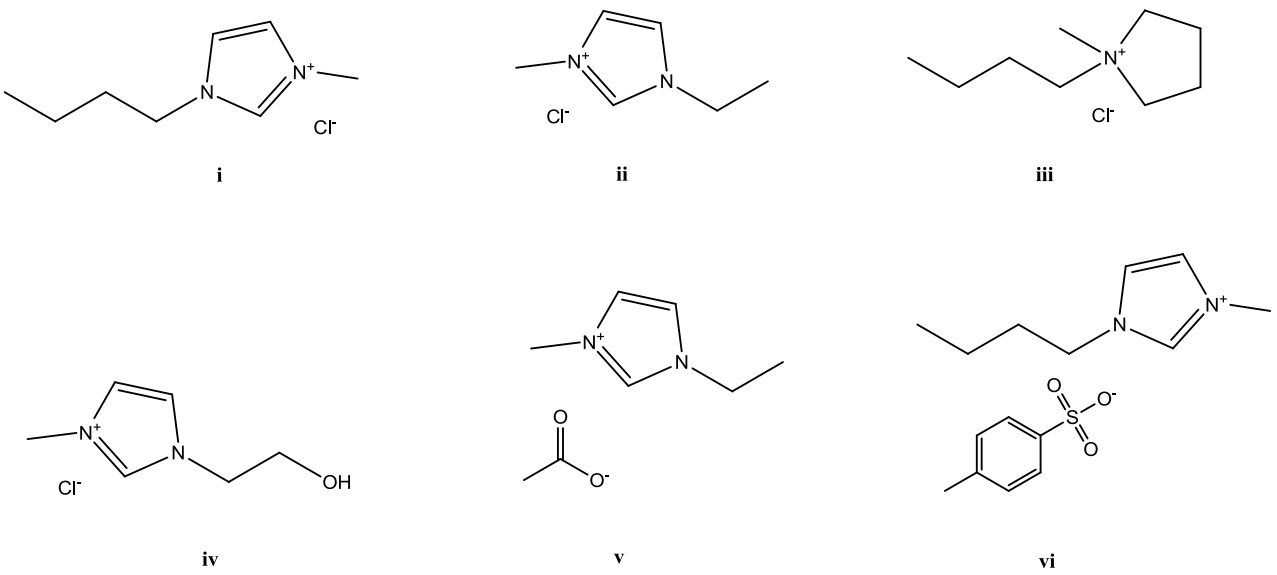

Fig. S1. Chemical structures of the ionic liquids used in the extraction of caffeine from guaraná seeds: (i) $[C_4mim]Cl$; (ii) $[C_2mim]Cl$; (iii) $[C_4mpyrr]Cl$; (iv) $[OHC_2mim]Cl$; (v) $[C_2mim][CH_3CO_2]$; (vi) $[C_4mim][Tos]$.

Table S1. 2^3 factorial planning.

Experiment	χ_1	χ_2	χ_3
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1.68	0	0
10	1.68	0	0
11	0	-1.68	0
12	0	1.68	0
13	0	0	-1.68
14	0	0	1.68
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Table S2. Coded levels of independents variables used in the first and second factorial planning.

Independent variables	Coded levels				
	Axial point -1.682	Factorial point -1	Central point 0	Factorial point +1	Axial point +1.682
Temperature (ºC)	36.4	50.0	70.0	90.0	104.0
Equilibrium time (minutes)	5.0	15.0	30.0	45.0	55.0
Solid-liquid ratio	0.04	0.07	0.10	0.20	0.27

Table S3. Experimental data and response surface values of the first RSM design using pure water.

Experiment	Temperature / ºC	Solid-liquid ratio	Time / min	Experimental yield of caffeine / wt%	Predicted yield of caffeine / wt%	Relative deviation / %
1	36.0	0.10	30.0	2.74	2.74	0.09
2	50.0	0.20	45.0	2.61	2.70	-3.38
3	50.0	0.20	45.0	2.87	2.72	5.39
4	50.0	0.20	15.0	2.64	2.71	-2.47
5	50.0	0.07	45.0	4.08	3.96	2.91
6	50.0	0.07	45.0	3.91	3.96	-1.26
7	50.0	0.07	15.0	3.82	3.89	-2.00
8	70.0	0.05	30.0	6.06	6.17	-1.83
9	70.0	0.05	30.0	6.31	6.18	1.96
10	70.0	0.10	5.0	3.62	3.45	4.63
11	70.0	0.10	5.0	3.63	3.48	4.17
12	70.0	0.10	55.0	4.24	4.40	-3.90
13	70.0	0.10	30.0	3.82	3.89	-1.73
14	70.0	0.10	30.0	3.90	3.84	1.45
15	70.0	0.10	30.0	3.86	3.86	-0.03
16	90.0	0.07	45.0	5.31	5.17	2.60
17	90.0	0.07	15.0	4.11	4.25	-3.39

Table S4. Regression coefficients of the predicted second-order polynomial model for the caffeine obtained from the first RSM design using pure water.

	Regression coefficients	Standard deviation	t-student (6)	P-value
Interception	**-1.51×10^{1}**	**4.26**	**-3.55**	**0.01**
Temperature	4.94×10^{-1}	0.08	5.85	<0.005
Temperature^2	-2.51×10^{-3}	0.00	-6.54	<0.005
Solid-liquid ratio	1.21×10^{2}	40.78	2.98	0.02
Solid-liquid ratio^2	-8.09×10^{1}	64.42	-1.26	0.26
Time	-2.96×10^{-2}	0.03	-1.08	0.32
Time^2	-2.41×10^{-5}	0.00	-0.10	0.93
Temperature × Solid-liquid ratio	-2.16×10^{0}	0.46	-4.66	<0.005
Solid-liquid ratio × Time	-2.79×10^{-2}	0.08	-0.36	0.73
Temperature × Time	7.04×10^{4}	0.00	2.65	0.04

Table S5. ANOVA data for the extraction of caffeine obtained from the first RSM design using pure water.

	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Regression	18.01	9	2.00	64.10	2.85×10^{-05}
Residuals	0.19	6	0.03		
Total	18.20				

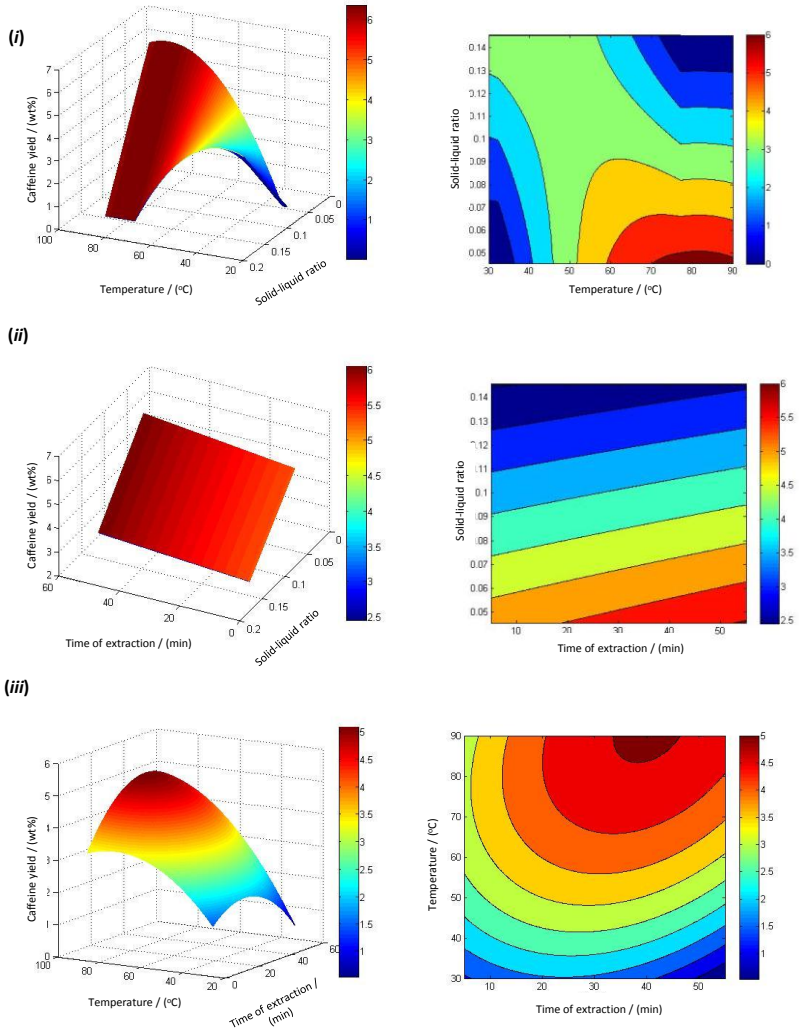

Fig. S2. Response surface plots (left) and contour plots (right) on the yield of caffeine with the combined effects of (*i*) temperature and solid-liquid ratio, (*ii*) time and solid-liquid ratio and (*iii*) temperature and time using pure water and guaraná particles with a diameter within 0.4 mm and 1.0 mm.

Table S6. Experimental data and response surface values of the second RSM design using [C_4mim]Cl aqueous solutions.

Experiment	Temperature / ºC	Solid-liquid ratio	Time / min	Experimental yield of caffeine / wt%	Predicted yield of caffeine / wt%	Relative deviation / %
1	36.0	0.10	30.0	3.39	3.39	0.02
2	50.0	0.20	45.0	5.32	5.50	-3.35
3	50.0	0.20	15.0	4.92	4.74	3.60
4	50.0	0.07	45.0	5.34	5.52	-3.39
5	50.0	0.07	15.0	5.16	4,98	3.51
6	70.0	0.04	30.0	8.39	8.39	-0.01
7	70.0	0.10	5.0	4.44	4.87	-9.69
8	70.0	0.10	55.0	7.19	6.76	5.99
9	70.0	0.10	30.0	6.03	6.10	-1.17
10	70.0	0.10	30.0	6.19	6.12	1.16
11	90.0	0.07	45.0	5.33	5.69	-6.73
12	90.0	0.07	15.0	4.43	4.07	8.09

Table S7. Regression coefficients of the predicted second-order polynomial model for the caffeine yield obtained from the second RSM design using [C_4mim]Cl aqueous solutions.

	Regression coefficients	Standard deviation	t-student (2)	P-value
Interception	**-3.76×10^{1}**	**17.74**	**-2.12**	**0.17**
Temperature	1.08×10^{0}	0.36	2.98	0.10
Temperature^2	-6.22×10^{-3}	0.00	-3.74	0.05
Solid-liquid ratio	2.55×10^{2}	168.68	1.51	0.27
Solid-liquid ratio ^{2}	-2.78×10^{2}	262.35	-1.06	0.40
Time	1.70×10^{-3}	0.11	0.02	0.99
Time^2	-5.20×10^{-4}	0.00	-0.53	0.65
Temperature × Solid-liquid ratio	-3.66×10^{0}	1.97	-1.86	0.20
Solid-liquid ratio × Time	4.72×10^{-2}	0.31	0.15	0.89
Temperature × Time	8.93×10^{-4}	0.00	0.88	0.47

Table S8. ANOVA data for the extraction of caffeine obtained from the second RSM design using [C_4mim]Cl aqueous solutions.

	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Regression	18.43	9	2.05	5.34	0.1675
Residuals	0.77	2	0.38		
Total	19.20				

Table S9. Coded levels of independents variables used in the third RSM design using [C_4mim]Cl aqueous solutions.

Variables	Coded levels				
	Axial point -1.682	Factorial point -1	Central point 0	Axial point -1.682	Factorial point -1
Temperature (ºC)	36.4	50.0	70.0	90.0	103.6
Concentration of ionic liquid (M)	0.66	1.00	1.50	2.00	2.34
Solid-liquid ratio	0.04	0.07	0.10	0.20	0.27

Table S10. Experimental data and response surface values of the third RSM design using $[C_4mim]Cl$ aqueous solutions.

Experiment	Temperature / ºC	Concentration / M	Time / min	Experimental yield of caffeine / wt%	Predicted yield of caffeine / wt%	Relative deviation / %
1	50.0	1.00	0.07	8.13	7.82	3.74
2	90.0	1.00	0.07	7.05	7.13	-1.18
3	50.0	2.00	0.07	9.04	8.59	4.97
4	90.0	2.00	0.07	8.59	8.56	0.29
5	50.0	1.00	0.10	6.28	7.16	-14.07
6	50.0	1.00	0.20	5.04	4.94	1.93
7	90.0	1.00	0.20	1.30	1.42	-9.33
8	50.0	1.00	0.20	8.78	8.72	0.65
9	50.0	1.00	0.10	7.94	8.70	-9.53
10	37.0	1.50	0.10	7.51	7.18	4.46
11	70.0	0.66	0.10	6.47	6.37	1.47
12	70.0	2.34	0.10	9.43	9.49	0.64
13	70.0	1.50	0.05	8.80	9.18	-4.33
14	70.0	1.50	0.10	8.18	8.17	0.02
15	70.0	1.50	0.10	8.37	8.18	2.24
16	70.0	1.50	0.10	8,29	8,19	1.30
17	70.0	1.50	0.10	8.21	8.19	0.27
18	70.0	1.50	0.10	8.34	8.22	1.38
19	70.0	1.00	0.10	7.49	7.16	4.42
20	70.0	0.50	0.10	6.01	5.97	0.60

Table S11. Regression coefficients of the predicted second-order polynomial models for extraction caffeine obtained from the second RSM design using [C_4mim]Cl aqueous solutions.

	Regression coefficients	Standard deviation	t-student (10)	P-value
Interception	**1.14×10^{0}**	**4.14**	**0.28**	**0.79**
Temperature	2.44×10^{-1}	0.07	3.31	0.01
Temperature ^{2}	-1.73×10^{-3}	0.00	-3.75	<0.005
Concentration	-4.91×10^{-1}	2.15	-0.23	0.82
Concentration^2	-3.56×10^{-1}	0.42	-0.85	0.41
Solid-liquid ratio	-1.21×10^{1}	25.59	-0.47	0.65
Solid-liquid ratio^2	-2.08×10^{-1}	58.79	-0.35	0.73
Temperature × Concentration	1.65×10^{-2}	0.02	0.85	0.41
Concentration × Solid-liquid ratio	2.26×10^{-1}	6.61	3.42	0.01
Temperature × Solid-liquid ratio	-5.33×10^{-1}	0.17	-3.22	0.01

Table S12. ANOVA data for the extraction of caffeine obtained from the third RSM design using [C_4mim]Cl aqueous solutions.

	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Regression	62.04	9	6.89	32.46	3.0797×10^{-06}
Residuals	2.12	10	0.21		
Total	64.16				