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 factorial planning, using water as solvent.

Studied parameters	Symbol	Level				
		Axial	**Factorial**	**Central**	**Factorial**	**Axial**
		-1.68	**-1**	**0**	**1**	**1.68**
Temperature (°C)	T	44.8	55.00	70.00	85.00	95.20
Time (min)	t	4.80	15.00	30.00	45.00	55.20
Solid-liquid ratio	R	0.05	0.07	0.10	0.13	0.05

Table S3. Coded levels of independents variables used in the second factorial planning, using [Ch][Bic] as solvent.

Studied parameters	Symbol	Level				
		Axial	**Factorial**	**Central**	**Factorial**	**Axial**
		-1.68	**-1**	**0**	**1**	**1.68**
Temperature (°C)	T	24.80	35.00	50.00	65.00	24.80
Concentration (M)	C	0.16	0.50	1.00	1.50	0.16
Solid-liquid ratio	R	0.05	0.07	0.10	0.13	0.05

Table S4. Experimental data and response surface predicted values of the factorial planning, using water as solvent.

Experiment	t (min)	T (°C)	Ratio S/L	Experimental caffeine yield (wt%)	Predicted yield caffeine yield (wt%)	Relative deviation (%)
1	15.00	55.00	0.09	1.10	1.47	4.53
2	15.00	85.00	0.07	1.33	2.01	2.10
3	45.00	55.00	0.07	1.07	1.49	-2.80
4	45.00	85.00	0.07	1.39	2.48	-1.37
5	15.00	55.00	0.13	1.00	1.30	2.25
6	15.00	85.00	0.13	1.08	1.70	2.98
7	45.00	55.00	0.13	1.09	1.32	-2.28
8	45.00	85.00	0.13	1.33	2.17	-3.74
9	30.00	44.80	0.10	1.04	1.32	-1.08
10	30.00	90.00	0.10	1.38	2.49	0.36
11	4.80	70.00	0.10	1.15	1.41	-7.44
12	55.20	70.00	0.10	1.04	1.82	6.61
13	30.00	70.00	0.05	1.34	1.92	-1.33
14	30.00	70.00	0.15	1.13	1.52	1.01
15	30.00	70.00	0.10	1.18	1.81	-0.53
16	30.00	70.00	0.10	1.17	1.81	-0.18
17	30.00	70.00	0.10	1.12	1.81	4.30
18	30.00	70.00	0.10	1.20	1.81	-2.51
19	30.00	70.00	0.10	1.16	1.81	1.35
20	50.00	70.00	0.10	1.20	1.81	-2.34

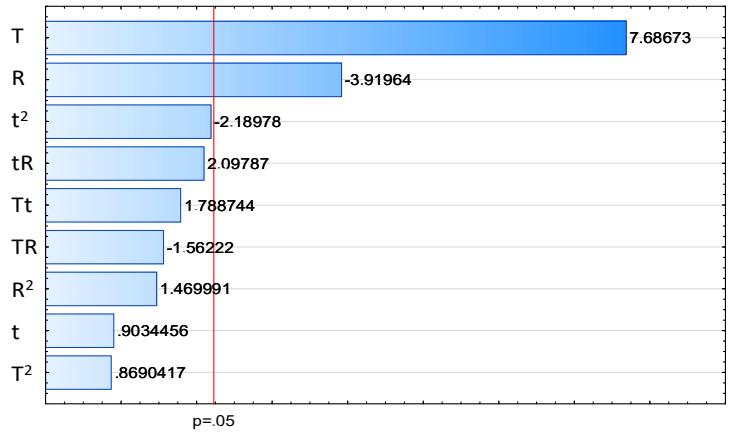

Figure S1. Pareto chart, using water as solvent. r^2 = 0.904; adj-r^2 = 0.817; p-value =0.000528.

T- temperature, R - solid-liquid ratio and t-time.

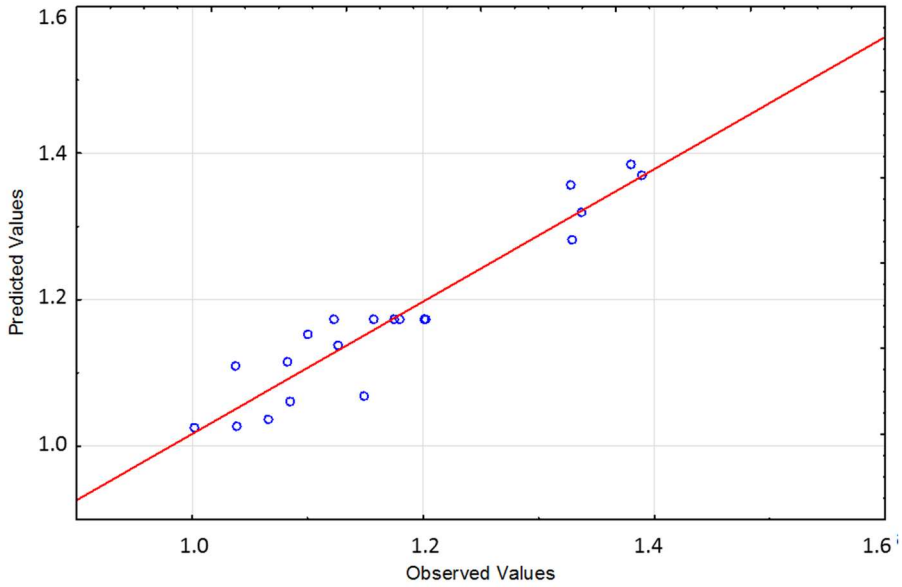

Figure S2. Predict *vs* observed values of caffeine yield (wt%) using water as solvent.

Table S5. Experimental data and response surface predicted values of the factorial planning, using [Ch][Bic] as solvent.

Experiment	T (°C)	C (M)	Ratio S/L	Experimental caffeine yield (wt%)	Predicted caffeine yield (wt%)	Relative deviation (%)
1	35.00	0.50	0.07	1.47	1.47	0.03
2	65.00	0.50	0.07	1.91	2.01	4.73
3	35.00	1.51	0.07	1.56	1.49	-4.47
4	65.00	1.51	0.07	2.48	2.48	0.07
5	35.00	0.50	0.13	1.28	1.30	1.59
6	65.00	0.50	0.13	1.61	1.70	5.23
7	35.00	1.51	0.13	1.39	1.32	-5.51
8	65.00	1.51	0.13	2.15	2.17	1.02
9	25.00	1.01	0.10	1.24	1.32	6.16
10	75.00	1.01	0.10	2.60	2.49	-4.54
11	50.00	0.16	0.10	1.52	1.41	-7.88
12	50.00	1.84	0.10	1.74	1.82	4.36
13	50.00	1.01	0.05	1.93	1.92	-0.39
14	50.00	1.00	0.15	1.54	1.52	-1.61
15	50.00	1.00	0.10	1.80	1.81	0.37
16	50.00	1.00	0.10	1.81	1.81	-0.04
17	50.00	1.00	0.10	1.82	1.81	-0.49
18	50.00	1.00	0.10	1.79	1.81	0.87
19	50.00	1.00	0.10	1.82	1.81	-0.46
20	50.00	1.00	0.10	1.81	1.81	0.07

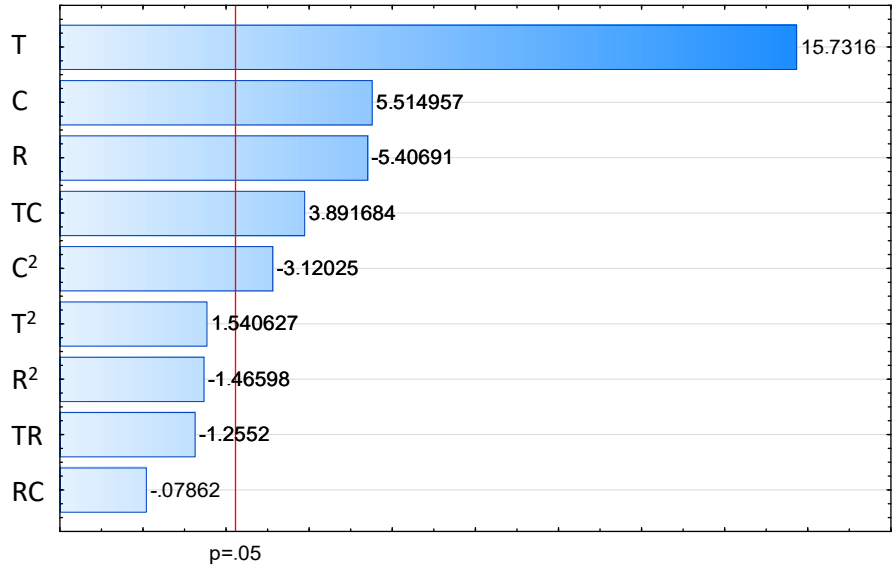

Figure S3. Pareto chart, using [Ch][Bic] as solvent. r^2 = 0.9713; adj-r^2 = 0.946; p-value =0,000002.

T - temperature, R -solid-liquid ratio and C - concentration of IL.

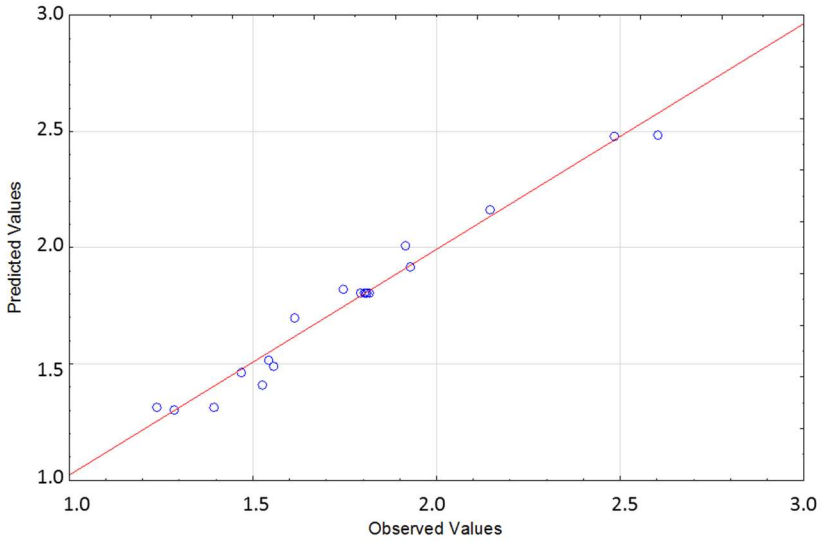

Figure S4. Predict *vs* observed values of caffeine yield (wt%) using [Ch][Bic] as solvent.

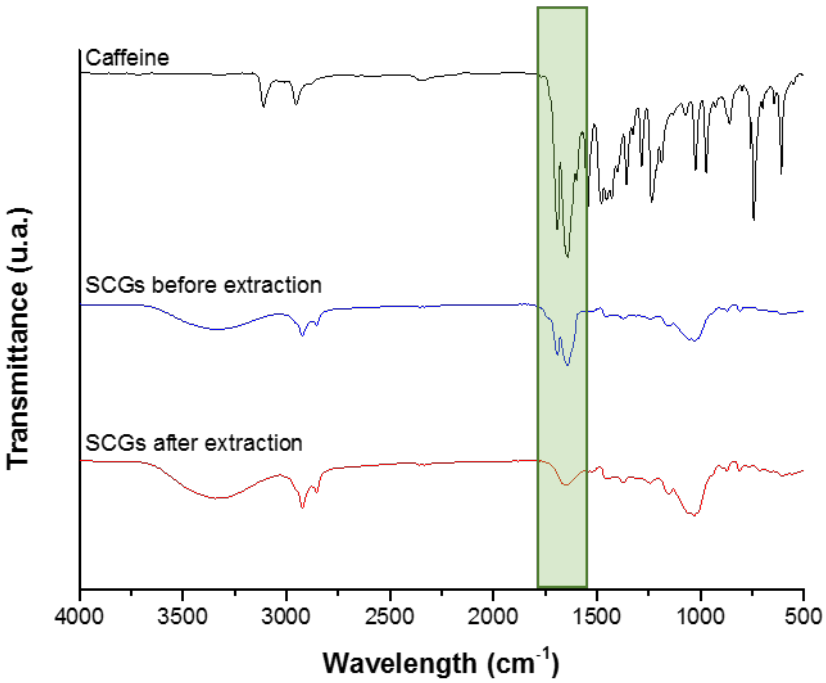

Figure S5. FTIR spectra of caffeine, SCGs sample before extraction, and SCGs samples after extraction using aqueous solution of [Ch][Bic] under the optimized operational conditions.

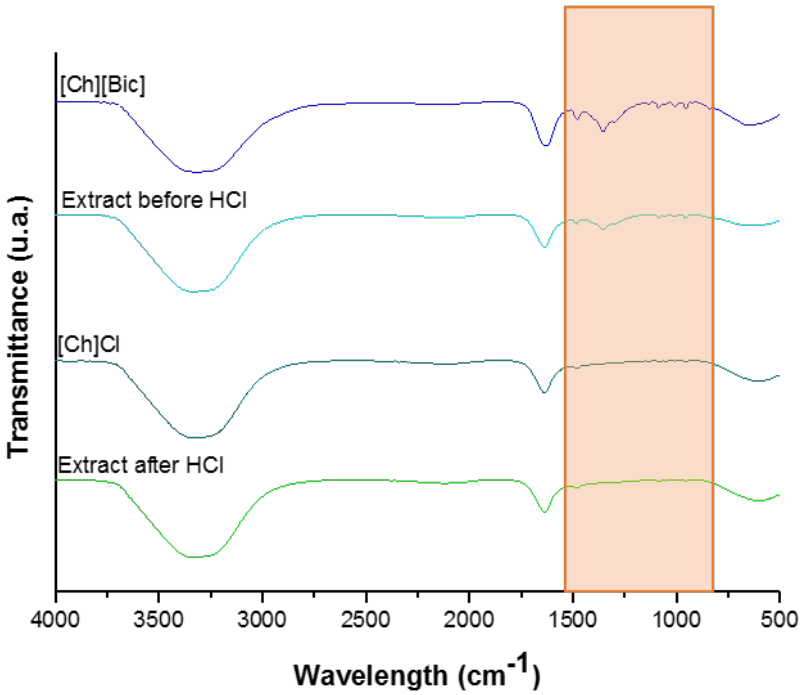

Figure S6. FTIR spectra corresponding to the pure ionic liquids, [Ch][Bic] and [Ch]Cl; and the extract obtained after six successive cycles, before and after addition of the HCl solution at 2 M.

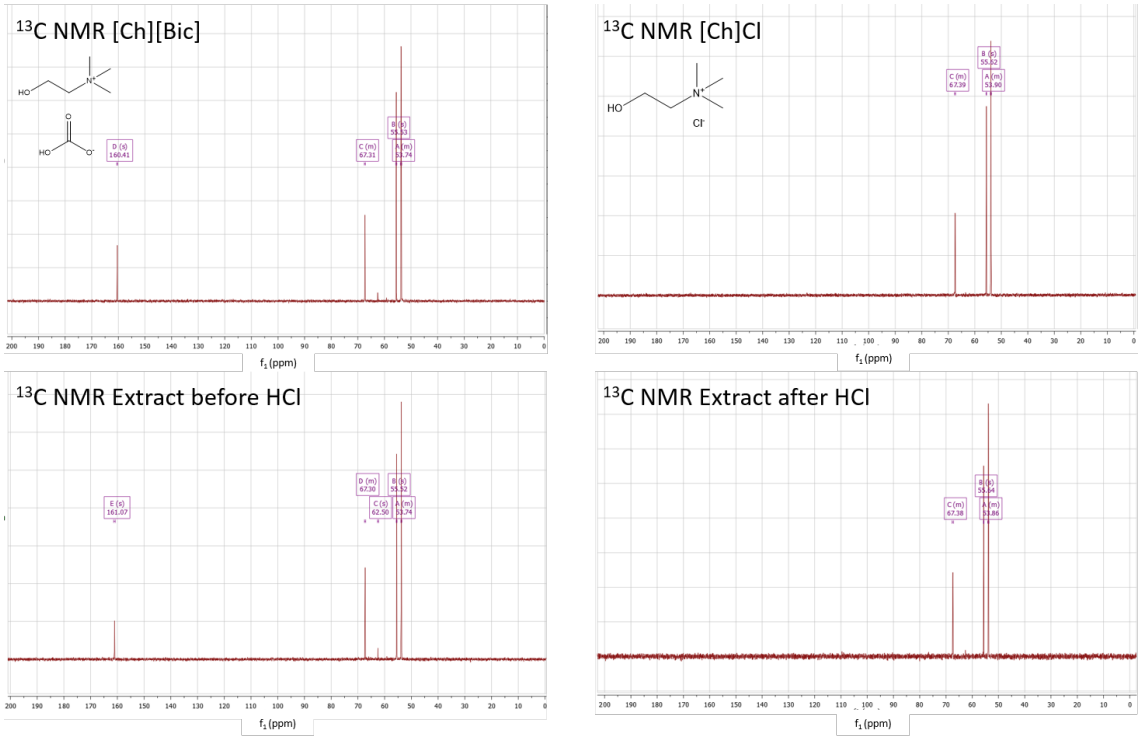

Figure S7. ^{13}C NMR spectra of the pure ionic liquids, [Ch][Bic] and [Ch]Cl; and the extract obtained after six successive cycles, before and after addition of the HCl solution at 2 M.