Supporting information

Recovery of syringic acid from industrial food waste with aqueous solutions of ionic liquids

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Surface response methodology

In a 2^k factorial planning there are k factors that can contribute to a response described by a second order polynomial equation:

$$y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j \quad \text{(S1)}$$

where y is the response variable (in this work, syringic acid extraction yield), β_0, β_i, β_{ii} and β_{ij} are the adjusted coefficients for the intercept, linear, quadratic and interaction terms, respectively, and X_i and X_j are independent variables. This mathematical model allows to obtain the response surface curves, and consequently to determine the optimized conditions of the process.

In this work was used a factorial planning 2^3 with the goal of optimizing the amount of extracted syringic acid from peel pears, as well as to identify the most significant parameters and their interaction. Three types of levels were considered: level zero (centre point), level one (1 and -1, factor points) and level α (axial points). The axial points are at an α-coded distance from the central point, as described by the following equation:

$$\alpha = (2^k)^{\frac{1}{4}} \quad \text{(S2)}$$

The central point is repeated because it gives information on the statistical interference between the data and parameters, and allows to determine the residuals and the standard error.

Figures/Tables

Table S1. 2^3 factorial planning.

	X_1	X_2	X_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. Solubility of syringic acid in aqueous solutions of ILs.

IL	IL concentration / (mol/L)	Solubility / (g/L)	SD[a]	S/S_0
$[C_4C_1im][TOS]$	0.00	1.43	0.08	1.00
	0.10	1.88	0.02	1.31
	0.25	2.38	0.02	1.66
	0.50	15.64	0.01	10.93
	0.75	25.12	0.15	17.56
	1.00	28.77	0.23	20.12
	2.00	37.13	0.01	25.97
	2.50	65.36	0.38	45.71
	3.00	0.65	0.19	0.46
$[C_4C_1im][N(CN)_2]$	0.10	4.41	0.01	3.09
	0.25	9.49	0.06	6.64
	0.50	25.12	0.03	17.56
	0.75	27.69	0.15	19.36
	1.00	31.60	0.01	22.10
	2.00	63.88	0.08	44.67
	2.50	57.51	0.06	40.22
	3.00	43.43	0.01	30.37
$[C_4C_1im]Cl$	0.10	2.05	0.01	1.43
	0.25	2.99	0.02	2.09
	0.50	5.06	0.01	3.54
	0.75	7.06	0.01	4.94
	1.25	15.35	0.05	10.73
	1.50	26.17	0.06	18.30
	2.00	34.82	0.08	24.35
	2.50	58.13	0.03	40.65
	3.00	92.00	0.07	64.34
	3.50	120.28	0.27	84.11
	4.00	50.60	0.29	35.38
$[C_4C_1im][HSO_4]$	0.10	1.88	0.01	1.31
	0.25	2.60	0.01	1.82
	0.50	4.43	0.01	3.10
	0.75	6.61	0.01	4.62
	1.00	9.47	0.26	6.62
	2.00	29.42	0.01	20.58
	2.50	11.27	0.01	7.88
$[C_4C_1im][SCN]$	0.10	2.19	0.02	1.53
	0.25	5.39	0.05	3.77
	0.50	6.54	0.03	4.57

	0.75	11.85	0.08	8.29
	1.00	32.52	0.29	22.74
	2.00	23.46	0.04	16.41
	2.50	21.58	0.05	15.09
	4.00	11.18	0.09	7.82
$[P_{4444}]Cl$	0.10	2.47	0.01	1.73
	0.25	4.32	0.01	3.02
	0.50	13.17	0.03	9.21
	0.75	28.78	0.13	20.13
	1.00	37.06	0.20	25.92
	2.00	52.21	0.05	36.51
	2.50	71.99	0.13	50.34
	3.00	63.68	0.47	44.53
$[N_{4444}]Cl$	0.10	4.35	0.01	3.05
	0.25	6.92	0.03	4.84
	0.50	9.13	0.01	6.38
	0.75	10.03	0.01	7.02
	1.00	14.09	0.08	9.85
	2.00	46.91	0.55	32.80
	2.50	41.48	0.01	29.00
	3.00	30.22	0.04	21.13
$[C_4C_1pip]Cl$	0.10	1.93	0.01	1.35
	0.25	2.23	0.01	1.56
	0.50	4.84	0.01	3.38
	0.75	7.34	0.05	5.13
	1.00	13.72	0.01	9.60
	2.00	15.77	0.06	11.02
	2.50	35.83	0.31	25.06
	3.00	70.68	0.15	49.43
	4.00	46.04	0.31	32.20
$[C_8C_1im]Cl$	0.25	7.80	0.03	5.46
	0.50	21.64	0.03	15.13
	0.75	28.32	0.13	19.80
	1.00	17.42	0.01	12.18
	2.00	16.54	0.05	11.56
	3.00	14.69	0.04	10.27
	3.50	6.59	0.05	4.61
$[C_4C_1im][CH_3CO_2]$	0.25	11.45	0.03	8.01
	0.50	24.21	0.19	16.93
	0.75	34.53	0.15	24.15
	1.00	40.17	0.31	28.09

	2.00	49.73	0.25	34.78
	3.00	72.75	0.21	50.87
	3.50	57.18	0.21	39.99
$[C_4C_1pyrr]Cl$	0.10	2.08	0.01	1.45
	0.25	3.46	0.01	2.42
	0.50	4.17	0.01	2.92
	0.75	5.60	0.01	3.92
	1.00	7.65	0.01	5.35
	2.00	15.91	0.08	11.12
	2.50	17.56	0.04	12.28
	3.00	12.45	0.03	8.71
$[C_4C_1py]Cl$	0.25	24.41	0.18	17.07
	0.50	33.92	0.15	23.72
	0.75	42.13	0.01	29.46
	1.00	53.79	0.09	37.61
	2.00	65.44	0.25	45.76
	3.00	75.28	0.05	52.64
	4.00	13.03	0.00	9.11
$[P_{i(444)1}][TOS]$	0.25	7.74	0.03	5.41
	0.75	28.59	0.33	19.99
	1.00	31.85	0.20	22.27
	2.00	38.00	0.43	26.57
	2.50	30.18	0.17	21.10
	3.00	22.18	0.14	15.51
[Ch]Cl	0.10	1.51	0.01	1.05
	0.25	1.64	0.01	1.15
	0.50	1.86	0.01	1.30
	0.75	1.97	0.01	1.38
	1.00	1.98	0.01	1.38
	2.00	2.35	0.01	1.64
[Ch][Ac]	0.25	14.43	0.11	10.09
	0.50	19.02	0.08	13.30
	0.75	20.50	0.33	14.34
	1.00	34.42	0.01	24.07
	2.00	34.53	0.33	24.15
	3.00	27.36	0.17	19.13
	3.50	17.59	0.13	12.30
[Ch][But]	0.10	7.68	0.01	5.37
	0.25	13.20	0.02	9.23
	0.50	19.58	0.17	13.69
	0.75	23.60	0.08	16.50

	1.00	27.60	0.25	19.30
	2.00	32.04	0.08	22.41
	2.50	41.11	0.25	28.75
	3.00	59.07	0.50	41.31
	3.50	23.92	0.12	16.73
[Ch][Hex]	0.25	23.20	0.06	16.22
	0.50	42.25	0.12	29.54
	0.75	59.07	0.34	41.31
	1.00	71.31	0.21	49.87
	2.00	85.69	0.28	59.92
	3.00	55.93	0.04	39.11
	4.00	1.74	0.05	1.22
[Ch][Oct]	0.25	20.77	0.13	14.53
	0.50	57.37	0.33	40.12
	0.75	62.23	0.16	43.52
	1.00	84.27	0.38	58.93
	2.00	57.91	0.50	40.50
	3.00	14.40	0.06	10.07
	3.50	5.41	0.05	3.79
[Ch][Dec]	0.10	18.28	0.02	12.78
	0.25	31.42	0.06	21.97
	0.50	24.86	0.03	17.38

[a]standard deviation in solubility results (in g/L)

Table S3. Coded levels of independents variables used in the first and second factorial planning.

	Axial -1.682	**Factorial -1**	**Central 0**	**Factorial 1**	**Axial 1.68**
Temperature (T, ºC)	29.8	38.0	50.0	62.0	70.16
Extraction time (t, min)	9.54	30.000	60.000	90.000	110.400
Solid-liquid ratio (R)	0.016	0.050	0.100	0.150	0.184

Table S4. Experimental data at the several conditions evaluated.

Experiment	T (ºC)	t (min)	Ratio S/L	Extraction yield of syringic acid (wt.%)
1	38.00	30.00	0.05	0.28
2	62.00	30.00	0.05	0.46
3	38.00	90.00	0.05	0.56
4	62.00	90.00	0.05	0.73
5	38.00	30.00	0.15	0.31
6	62.00	30.00	0.15	0.53
7	38.00	90.00	0.15	0.26
8	62.00	90.00	0.15	0.34
9	29.82	60.00	0.10	0.99
10	70.16	60.00	0.10	0.78
11	50.00	9.54	0.10	0.36
12	50.00	110.40	0.10	0.86
13	50.00	60.00	0.02	0.57
14	50.00	60.00	0.18	0.80
15	50.00	60.00	0.10	1.05
16	50.00	60.00	0.10	0.87
17	50.00	60.00	0.10	0.96
18	50.00	60.00	0.10	0.91
19	50.00	60.00	0.10	0.87
20	50.00	60.00	0.10	1.01

Table S5. Regression coefficients of the predicted second-order polynomial model for the syringic acid extraction yield obtained from the RSM. The statistical results obtained are in terms of the coded values of the factors.

	Regression coefficients	Standard deviation	t-student (10)	P-value
Interception	-2.5693	1.4106	-1.8214	0.0985
(1) T (ºC) (L)	0.0614	0.0431	1.4233	0.1851
T^2 (ºC) (Q)	-0.0006	0.0004	-1.4237	0.1850
(2) t (min) (L)	0.0354	0.0140	2.5383	0.0594
t^2 (min) (Q)	-0.0002	0.0001	-3.1398	0.0105
(3) Solid-liquid ratio(L)	16.2429	8.3703	1.9405	0.0810
Solid-liquid ratio^2 (Q)	-60.7552	22.4770	-2.7030	0.0222
1L by 2L	-0.0001	0.0002	-0.2430	0.8129
1L by 3L	-0.0089	0.1256	-0.0708	0.9449
2L by 3L	-0.0659	0.0502	-1.3121	0.2188

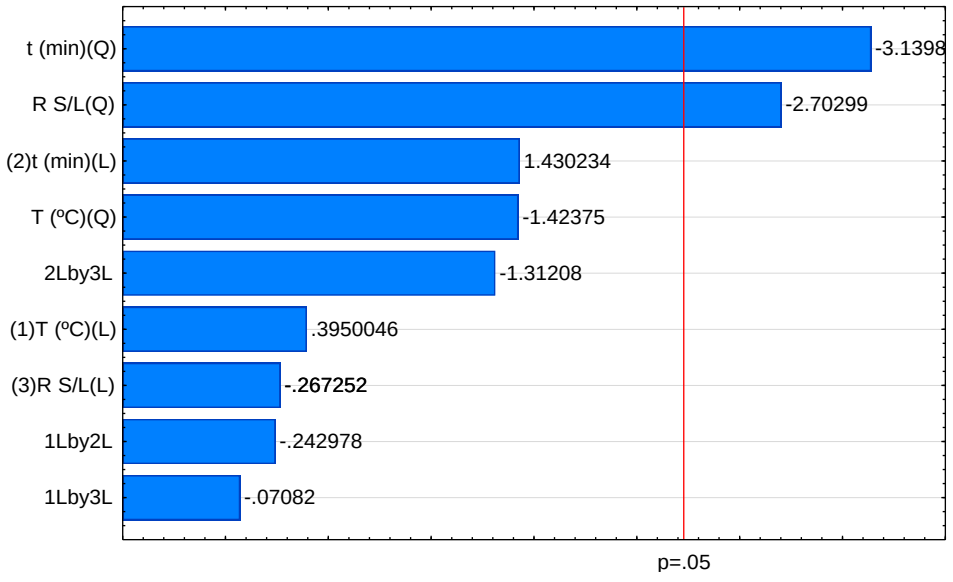

Figure S1. Pareto chart for the standardized main effects in the factorial planning for the syringic acid extraction yield. The vertical line indicates the statistical significance of the several effects.

Table S6. Syringic acid extraction yield according to the biomass reuse at the best conditions (T = 50ºC, t = 60 min and S/L ratio = 0.10, using aqueous solutions of [C_4C_1im]Cl at 3.5 M).

Nº of extraction cycle	Syringic acid total yield (wt.%)
1st	1.05
2nd	0.49
3rd	0.39
4th	0.24
5th	0.05
Total	**2.22**

Table S7. Syringic acid extraction yield according to the reusability of the aqueous solution of [C_4C_1im]Cl at 3.5 M.

Nº of extraction cycle	Syringic acid total yield (wt.%)
1st	1.07
2nd	0.44
3rd	0.24
4th	0.19
5th	0.09
Total	2.04

Table S8. Amount of water (mL) added and percentage of precipitation of syringic acid.

Amount of water (mL)	Syringic acid precipitation (%)
1	6.98
5	18.60
10	30.23
15	51.16
25	76.74

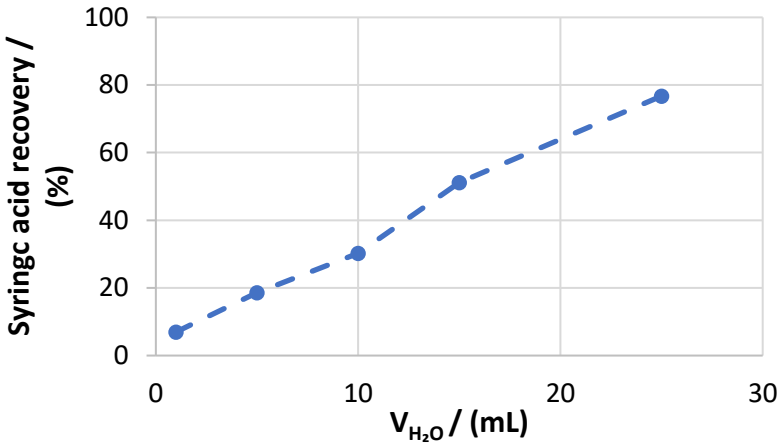

Figure S2. Amount of water (mL) added and percentage of precipitation/recovery of syringic acid to 0.5 mL of the IL aqueous solution after the extraction.

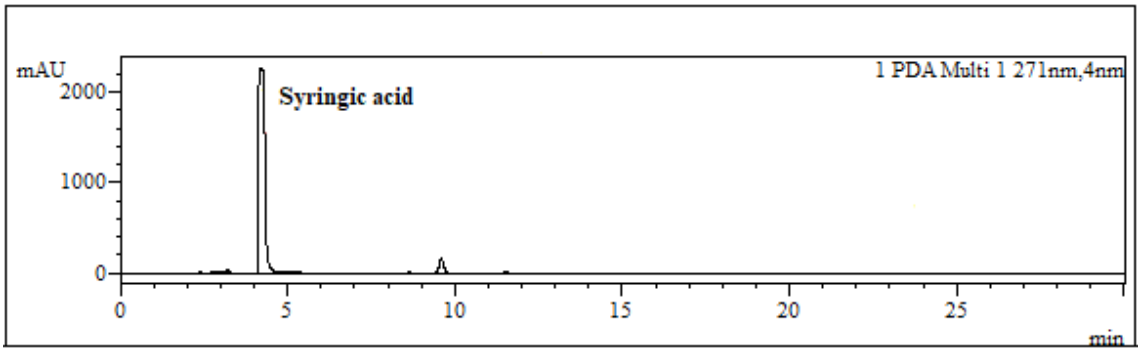

Figure S3. HPLC-DAD chromatogram of the precipitated sample from the IL aqueous solution after the addition of water.