Supporting Information

Silica-supported ionic liquids as efficient materials to separate cobalt and nickel from lithium in aqueous solutions

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Synthesis of the imidazolium-based SIL ([Si][C_3C_1Im]Cl)

Commercial silica-gel, with a pore size of 90 Å, was immersed in hydrochloric acid for 24 h, to enhance the content of silanol groups on the particles surface. Then, the particles were washed with double distilled water and dried for 24 h at 60 ºC. A second step followed, involving the suspension of the activated silica (5.0 g) in 50 mL of dried toluene, followed by the addition of 3-chloropropyltrimethoxysilane (5.0 mL). The suspension was refluxed under mechanic stirring for 24 h at 100 °C. The chloropropyl silica obtained, [Si][C_3]Cl, was transferred to a vacuum glass filter, washed with toluene (100 mL), 1:1 ethanol–water mixture (200 mL), double distilled water (500 mL) and methanol (100 mL), and then dried for 24 h at 60 ºC. The last step consisted on the suspension of [Si][C_3]Cl (5.0 g) in 50 mL of dried toluene, followed by the addition of *N*-methylimidazole (5.0 mL). The suspension was refluxed under mechanic stirring for 24 h at 110 °C. The obtained material, [Si][C_3C_1Im]Cl, was transferred to a vacuum glass filter, washed with toluene (100 mL), methanol (350 mL), double distilled water (300 mL) and methanol (150 mL), and then dried for 24 h at 60 ºC.

Elements quantification

The amount of lithium, cobalt and nickel was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), on a Horiba Jobin Yvon Activa M spectrometer (radial configuration) equipped with a Burgener MiraMist nebulizer (sample flow of 1 mL/min), peristaltic sample delivery pump with three canals, argon flow (nebulizer: 0.02 L/min; auxiliary gas: 0.2 L/min; plasma: 12 L/min), nebulizer chamber, CCD (coupled charging device) for detection, and algorithm background correction for quantification. Calibration curves were stablished using 5 standards with concentrations between 20 and 2000 µg/L prepared by the dilution of Li, Co and Ni standard solutions into acidified water (1 % HNO_3 v/v). Only calibration curves with a correlation coefficient above 0.999 were used. The limit of quantification was considered as the lowest standard of the calibration curve (20 µg/L). The coefficient of variation between sample replicates (at least, three replicates were investigated) did not exceed 5 %.

The removal efficiency, R (%), for Li, Co and Ni by the SIL was determined according to Equation (S1):

$$\text{Removal}\ (\%) = \frac{(\mathrm{C_0} - \mathrm{C_t})}{\mathrm{C_0}} * 100 \qquad \text{(S1)}$$

where $\mathrm{C_0}$ (µg/L) is the initial concentration of metals in solution and $\mathrm{C_t}$ (µg/L) is the concentration of metals at time t.

RSM equations

RSM substitutes the real values of independent variables (X_k) by codified values, according to the equation represented below:

$$\mathrm{X}_k = \frac{(\mathrm{x}_k - \mathrm{x}_0)}{\Delta \mathrm{x}_k} \qquad \text{(S2)}$$

where x_k corresponds to the uncodified value of the independent variables, x_0 is the variable value at its centre point, and $\Delta \mathrm{x}_k$ is the step change between levels for the k variable. The codified variables have a mean of zero and a standard deviation of one, which simplifies the analysis.

The linear, quadratic and combined effects of variables are described through a second order polynomial function (expressed by Equation (S3)) that allows to predict the optimized conditions.

$$\mathrm{Y} = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_{ii} \mathrm{X}_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j \qquad \text{(S3)}$$

where Y is the response variable studied, X_i, X_j, … X_k are codified values of the independent variables, β_0 is a constant, β_i, β_{ii}, and β_{ij} are the regression coefficients for the linear, quadratic, and interaction terms [1–3].

Design-Expert version 13 (Stat-Ease Inc.) and Minitab Statistical Software version 19 were the software used for obtaining the results. The significance of the factors was assessed through analysis of variance (ANOVA), while to evaluate the interactions between the factors Fisher's test and its associated probability p(F) were used. The coefficient of determination, R^2 (Equation (S4)), and the adjusted coefficient of determination, R^2_{adj} (Equation (S5)), allowed to check the fitting:

$$\mathrm{R}^2 = 1 - \frac{\sum(\hat{y}_i - y_i)^2}{\sum(y_i - \bar{y})^2} \qquad \text{(S4)}$$

$$\mathrm{R}^2_{adj} = 1 - (1 - \mathrm{R}^2)\frac{(\mathrm{N_{DP}} - 1)}{(\mathrm{N_{DP}} - \mathrm{N_P} - 1)} \qquad \text{(S5)}$$

where $\hat{y}_i$ are the values calculated by the model obtained, y_i are the experimental values, $\bar{y}$ is the mean of the experimental values, N_{DP} is the number of experimental data points, and N_P is the number of parameters.

Extraction procedure

For the extraction procedure, the appropriate buffer for each assay was added to the tissue samples at a ratio of 1:2 (w/v). To determine the ETS activity, samples were extracted with Tris-HCl buffer 0.1 mol/L at pH 8.5 with 15% (w/v) PVP, 153 µmol/L magnesium sulphate ($MgSO_4$) and 0.2% (v/v) Triton X-100. For PROT and SOD the potassium phosphate buffer 50 mmol/L at pH 7.0 with 1 mmol/L EDTA, 1 % (v/v) Triton X-100 and 1 mmol/L DTT was used for sample extraction. To determine LPO levels, the extraction buffer was 20 % (w/v) trichloroacetic acid (TCA). Samples were homogenized using a TissueLyzer II (Qiagen) set at a frequency of 20 1/s for 90 s, and afterwards centrifuged for 20 min at 4 ºC at 10 000 *g* (only for ETS they were centrifuged at 3 000 *g*). The supernatant was immediately collected and kept at -80 ºC until use for biomarkers quantification.

Tables

Table S1. Description of the experimental conditions according to the Box-Behnken design.

Experiment	pH	Dose of sorbent (g/L)	Initial concentration of Li, Co and Ni (mg/L)
1	6	1.0	1.2
2	8	1.0	0.4
3	4	1.0	0.4
4	6	1.0	1.2
5	4	1.5	1.2
6	8	1.0	2.0
7	6	1.5	0.4
8	6	1.5	2.0
9	6	0.5	0.4
10	8	1.5	1.2
11	4	0.5	1.2
12	6	0.5	2.0
13	6	1.0	1.2
14	8	0.5	1.2
15	4	1.0	2.0

Table S2. Removal (%) of Li, Co and Ni achieved by the SIL [Si][C_3C_1Im]Cl, after 2 h of sorption, under the experimental conditions presented in Table S1.

Experiment	pH	Dose of sorbent (g/L)	Initial concentration of Li, Co and Ni (mg/L)	Removal (%)		
				Li	Co	Ni
1	6	1.0	1.2	0	71	76
2	8	1.0	0.4	0	86	93
3	4	1.0	0.4	0	28	61
4	6	1.0	1.2	0	71	76
5	4	1.5	1.2	0	53	78
6	8	1.0	2.0	0	49	57
7	6	1.5	0.4	0	73	93
8	6	1.5	2.0	0	73	79
9	6	0.5	0.4	0	73	79
10	8	1.5	1.2	0	77	82
11	4	0.5	1.2	0	38	54
12	6	0.5	2.0	0	45	52
13	6	1.0	1.2	0	70	75
14	8	0.5	1.2	0	44	50
15	4	1.0	2.0	0	54	69

Table S3. Analysis of variance of the effects of variables in the removal efficiency of Co at 2 h of exposure.

	Sum of squares	**df**	**Mean square**	**F-value**	**p-value**
Model	3825.65	9	425.07	13.61	0.0051
A-pH	848.77	1	848.77	27.18	0.0034
B-Dose of sorbent	720.37	1	720.37	23.07	0.0049
C-Concentration	179.16	1	179.16	5.74	0.0620
AB	89.83	1	89.83	2.88	0.1506
AC	993.91	1	993.91	31.83	0.0024
BC	192.20	1	192.20	6.15	0.0558
A^2	790.06	1	790.06	25.30	0.0040
B^2	29.40	1	29.40	0.9414	0.3765
C^2	10.28	1	10.28	0.3291	0.5910
Residual	156.14	5	31.23		
Lack of Fit	155.75	3	51.92	263.21	0.0038
Pure Error	0.3945	2	0.1972		
Cor Total	3981.79	14			

Table S4. Analysis of variance of the effects of variables in the removal efficiency of Ni at 2 h of exposure.

	Sum of squares	**df**	**Mean square**	**F-value**	**p-value**
Model	2555.60	9	283.96	14.38	0.0045
A-pH	55.55	1	55.55	2.81	0.1544
B-Dose of sorbent	1154.81	1	1154.81	58.47	0.0006
C-Concentration	580.21	1	580.21	29.38	0.0029
AB	20.13	1	20.13	1.02	0.3590
AC	461.72	1	461.72	23.38	0.0047
BC	35.43	1	35.43	1.79	0.2381
A^2	214.43	1	214.43	10.86	0.0216
B^2	13.91	1	13.91	0.7045	0.4396
C^2	14.49	1	14.49	0.7336	0.4309
Residual	98.76	5	19.75		
Lack of Fit	98.30	3	32.77	141.55	0.0070
Pure Error	0.4630	2	0.2315		
Cor Total	2654.36	14			

Figures

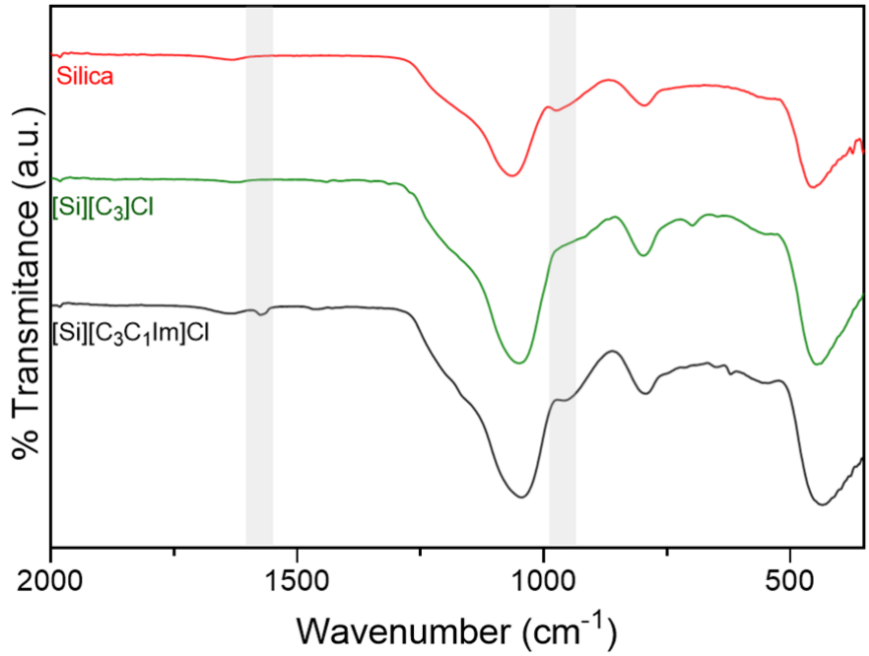

Figure S1. FTIR spectra of activated silica-gel (red line), [Si][C_3]Cl (green line) and [Si][C_3C_1Im]Cl (black line).

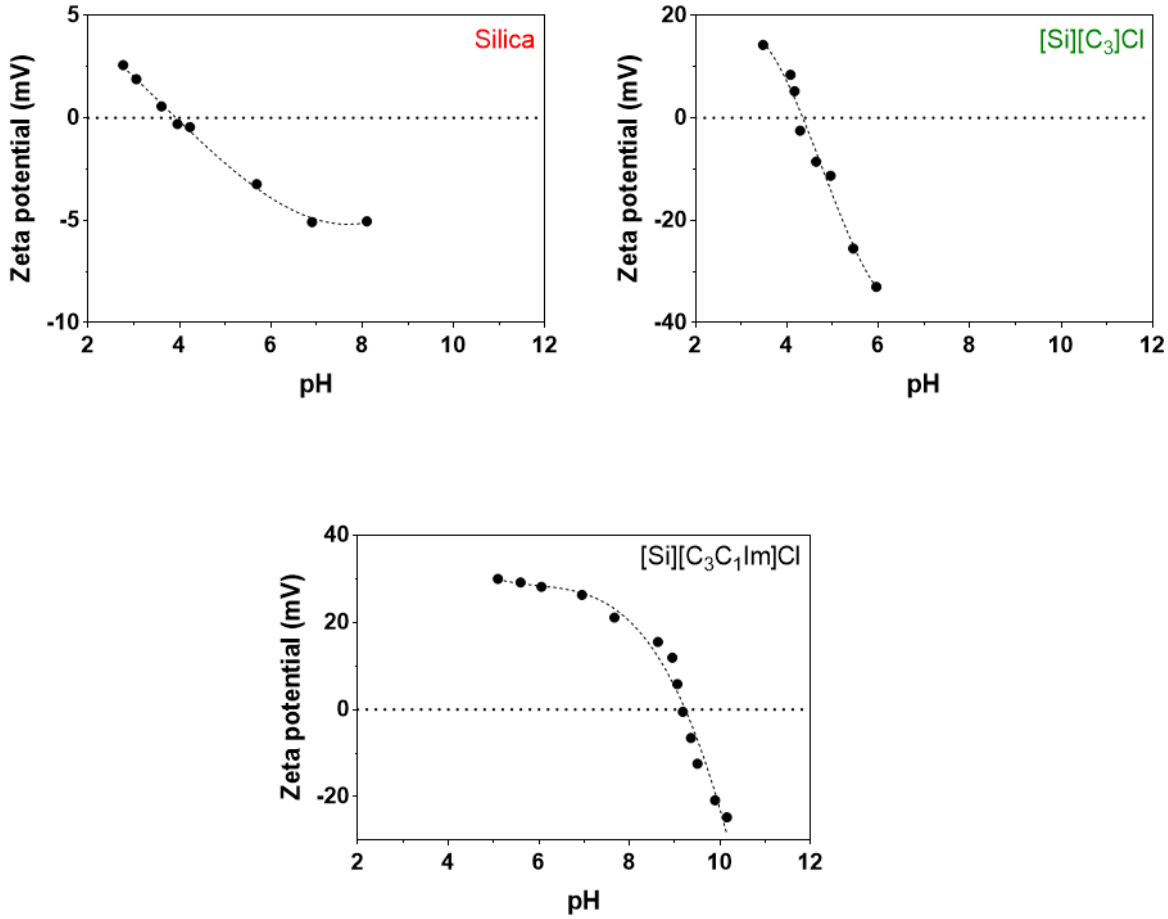

Figure S2. Zeta potential as a function of pH for the activated silica-gel, [Si][C_3]Cl and [Si][C_3C_1Im]Cl.

References cited in the Supporting Information

[1] A. Witek-Krowiak, K. Chojnacka, D. Podstawczyk, A. Dawiec, K. Pokomeda, Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process, Bioresour. Technol. 160 (2014) 150–160.

[2] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Box-Behnken design: An alternative for the optimization of analytical methods, Anal. Chim. Acta. 597 (2007) 179–186.

[3] E. Fabre, B. Henriques, T. Viana, J. Pinto, M. Costa, N. Ferreira, D. Tavares, C. Vale, J. Pinheiro-Torres, E. Pereira, Optimization of Nd(III) removal from water by Ulva sp. and Gracilaria sp. through Response Surface Methodology, J. Environ. Chem. Eng. 9 (2021) 105946–105954.