Supplementary Materials

First Stage of the Development of an Eco-Friendly Detergent Formulation for Efficient Removal of Carbonized Soil

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In this work, the commercial degreaser KH7, from KH Lloreda company, was used. This degreaser is composed of water, fatty ethoxylated alcohol, methoxypropanol, monoethanolamine and polycarboxylate with a pH of 11.25.

Tables

**Table S1.** pH of the different formulations used in the screening.

| Surfactant | Solvent | PM  | DPM | BDG  | MMB  | IPG  |
|------------|---------|-----|-----|------|------|------|
| [N\(_{118}\)][C\(_{8}\)O\(_2\)] |             | 10.36 | 7.91 | 8.53  | 8.54  | 10.26 |
| [N\(_{118}\)][C\(_{10}\)O\(_2\)] |             | 8.87 | 8.20 | 8.28  | 8.28  | 8.75  |
| [N\(_{118}\)][C\(_{12}\)O\(_2\)] |             | 9.02 | 8.48 | 9.06  | 8.84  | 8.97  |
| [N\(_{1110}\)][C\(_{8}\)O\(_2\)] |             | 10.19 | 8.32 | 9.82  | 7.86  | 10.38 |
| [N\(_{1110}\)][C\(_{10}\)O\(_2\)] |             | 9.21 | 8.45 | 8.83  | 8.83  | 9.06  |
| [N\(_{1110}\)][C\(_{12}\)O\(_2\)] |             | 9.30 | 8.56 | 8.33  | 8.10  | 9.34  |
| [N\(_{1112}\)][C\(_{10}\)O\(_2\)] |             | 9.35 | 8.39 | 8.75  | 9.15  | 9.25  |
| [N\(_{1112}\)][C\(_{12}\)O\(_2\)] |             | 9.65 | 8.62 | 9.00  | 9.30  | 9.46  |
| C\(_{12}-C_{15}\) 7EO's |         | 5.08 | 4.15 | 4.99  | 4.05  | 5.11  |
| C\(_{10}\) 6EO's |             | 4.68 | 4.04 | 4.67  | 3.18  | 4.54  |
| C\(_{12}-C_{15}\) 9EO's |         | 5.80 | 4.30 | 5.94  | 4.19  | 5.43  |
| C\(_{11}-C_{13}\) 9EO's |         | 5.07 | 3.95 | 4.99  | 3.90  | 4.71  |
| C\(_{10}-C_{14}\) 8EO's |         | 5.10 | 4.05 | 4.86  | 3.98  | 5.04  |
Table S2. *HLB* values of nonionic surfactants, given by the suppliers.

| Nonionic surfactant | HLB |
|---------------------|-----|
| C<sub>10</sub> 6EO’s | 12.4 |
| C<sub>11</sub>-C<sub>13</sub> 9EO’s | 13.2 |
| C<sub>12</sub>-C<sub>15</sub> 7EO’s | 12.3 |
| C<sub>12</sub>-C<sub>15</sub> 9EO’s | 13.1 |
| C<sub>10</sub>-C<sub>14</sub> 8EO’s | 13.6 |

Table S3. Mixture design for optimization of the solvent composition.

| Run | Coded variables | Surfactant (wt%) | Solvent (wt%) | Water (wt%) |
|-----|-----------------|-----------------|--------------|------------|
| 1   |                 | 10.00           | 13.00        | 77.00      |
| 2   |                 | 10.00           | 3.00         | 87.00      |
| 3   |                 | 3.00            | 13.00        | 84.00      |
| 4   |                 | 3.00            | 3.00         | 94.00      |
| 5   |                 | 3.00            | 8.00         | 89.00      |
| 6   |                 | 10.00           | 8.00         | 82.00      |
| 7   |                 | 6.50            | 3.00         | 90.50      |
| 8   |                 | 6.50            | 13.00        | 80.50      |
| 9   |                 | 6.50            | 8.00         | 85.50      |
Table S4. pH and efficiency obtained for the formulations used in the mixture design of C11-C13 9EO’s, IPG and water.

Model for ceramic: $R^2 = 0.97$ and $R^2_{adj} = 0.91$

Model for stainless-steel: $R^2 = 0.80$ and $R^2_{adj} = 0.47$

| Run | pH  | Experimental Efficiency | Predicted Efficiency |
|-----|-----|-------------------------|---------------------|
|     |     | Ceramic | Stainless-steel | Ceramic | Stainless-steel |
| 1   | 4.24| 0.45   | 0.65          | 0.42    | 0.61          |
| 2   | 4.09| 0.76   | 0.87          | 0.79    | 0.80          |
| 3   | 4.24| 1.02   | 0.87          | 0.99    | 0.93          |
| 4   | 4.18| 0.60   | 0.90          | 0.62    | 0.92          |
| 5   | 4.19| 0.90   | 0.90          | 0.90    | 0.83          |
| 6   | 4.15| 0.70   | 0.51          | 0.70    | 0.61          |
| 7   | 4.30| 0.93   | 0.82          | 0.87    | 0.86          |
| 8   | 4.20| 0.82   | 0.80          | 0.87    | 0.78          |
| 9   | 4.14| 0.96   | 0.74          | 0.97    | 0.72          |
Table S5. pH and efficiency obtained for the formulations used in the mixture design of [N\textsubscript{1118}][C\textsubscript{8}O\textsubscript{2}], BDG and water.

Model for ceramic: $R^2 = 0.94$ and $R^2_{\text{adj}} = 0.84$

Model for stainless-steel: $R^2 = 0.92$ and $R^2_{\text{adj}} = 0.80$

| Run | pH  | Experimental Efficiency | Predicted Efficiency |
|-----|-----|-------------------------|----------------------|
|     |     | Ceramic | Stainless-steel | Ceramic | Stainless-steel |
| 1   | 8.23| 0.87    | 1.10         | 0.83    | 1.06          |
| 2   | 8.74| 0.63    | 0.95         | 0.65    | 0.93          |
| 3   | 7.58| 0.47    | 1.03         | 0.41    | 0.99          |
| 4   | 7.92| 0.32    | 0.41         | 0.31    | 0.40          |
| 5   | 7.70| 0.25    | 0.65         | 0.33    | 0.70          |
| 6   | 8.41| 0.68    | 0.93         | 0.70    | 0.99          |
| 7   | 7.83| 0.87    | 0.68         | 0.87    | 0.71          |
| 8   | 8.05| 0.90    | 0.98         | 1.00    | 1.06          |
| 9   | 8.15| 1.00    | 1.00         | 0.90    | 0.89          |
Table S6. ANOVA for the mixture design using formulations composed of C_{11}-C_{13} 9EOs, IPG and water applied to the ceramic surface.

|                | SS     | df  | MS      | F         | P       |
|----------------|--------|-----|---------|-----------|---------|
| Model (Regression) | 0.265929 | 5   | 0.053186 | 17.30503  | 0.020203 |
| Total Error (Residual) | 0.009220 | 3   | 0.003073 |           |         |
| Total Adjusted    | 0.275149 | 8   | 0.034394 |           |         |

Table S7. ANOVA for the mixture design using formulations composed of C_{11}-C_{13} 9EOs, IPG and water applied to the stainless-steel surface.

|                | SS     | df  | MS      | F         | P       |
|----------------|--------|-----|---------|-----------|---------|
| Model (Regression) | 0.110659 | 5   | 0.022132 | 3.399777  | 0.051053 |
| Total Error (Residual) | 0.027667 | 3   | 0.009222 |           |         |
| Total Adjusted    | 0.138327 | 8   | 0.017291 |           |         |
Table S8. Efficiency and pH obtained for the optimal composition of the formulation composed of C\textsubscript{11}-C\textsubscript{13} 9EO’s, IPG and water.

| Surface        | Optimal composition | Efficiency | Relative deviation (%) | pH  |
|----------------|---------------------|------------|------------------------|-----|
|                | IPG  | C\textsubscript{11}-C\textsubscript{13} 9EO’s | H\textsubscript{2}O | Experimental | Predicted |               |
| Ceramic        | 10.0 | 5.0          | 85.0        | 1.03         | 1.00       | 3.00 | 4.30 |
| Stainless-steel| 13.0 | 3.0          | 84.0        | 0.95         | 0.91       | 4.40 | 4.24 |

Table S9. ANOVA for the mixture design using formulations composed of [N\textsubscript{1118}][C\textsubscript{8}O\textsubscript{2}], BDG and water applied to the ceramic surface.

|                      | SS              | df | MS          | F              | p     |
|----------------------|-----------------|----|-------------|----------------|-------|
| Model (Regression)   | 0.54402678      | 5  | 0.108805    | 9.313672       | 0.04783 |
| Total Error (Residual)| 0.03504698    | 3  | 0.011682    |                |       |
| Total Adjusted       | 0.57907375      | 8  | 0.072384    |                |       |
Table S10. ANOVA for the mixture design using formulations composed of [N\textsubscript{1118}][C\textsubscript{8}O\textsubscript{2}], BDG and water applied to the stainless-steel surface.

|                      | SS      | df | MS      | F        | p         |
|----------------------|---------|----|---------|----------|-----------|
| Model (Regression)   | 0.381089| 5  | 0.076218| 7.227412 | 0.047155  |
| Total Error (Residual) | 0.031637| 3  | 0.010546|          |           |
| Total Adjusted       | 0.412726| 8  | 0.051591|          |           |

Table S11. Efficiency and pH obtained for the optimal composition of the formulation composed of [N\textsubscript{1118}][C\textsubscript{8}O\textsubscript{2}], BDG and water.

| Surface             | Optimal composition | Efficiency | Relative deviation (%) | pH  |
|---------------------|---------------------|------------|------------------------|-----|
|                     | BDG | [N\textsubscript{1118}][C\textsubscript{8}O\textsubscript{2}] | H\textsubscript{2}O | Experimental | Predicted |          |  |
| Ceramic             | 13.0 | 7.0 | 80.0 | 0.99 | 1.03 | 3.90 | 8.28 |
| Stainless-steel     | 13.0 | 8.0 | 79.0 | 1.04 | 1.07 | 2.80 | 8.63 |
Figures

Figure S1. Contact angles of net and soiled surfaces: (a) ceramic and (b) stainless-steel.

Figure S2. Predict vs. observed values of IPG + C_{11}-C_{13} 9EO’s for soil’s removal from (A) ceramic and (B) stainless-steel.
Figure S3. Pareto charts for the standardized main effects in the IPG + C_{11}-C_{19} 9EO’s mixture design for (A) ceramic and (B) stainless-steel. The vertical line indicates the statistical significance of the effects (95% of confidence).

Figure S4. Predict vs. observed values of BDG + [N_{1118}][C_{8}O_{2}] for soil’s removal from (A) ceramic and (B) stainless-steel.
Figure S5. Pareto charts for the standardized main effects in the BDG + [N111][CsO2] mixture design for (A) ceramic and (B) stainless-steel. The vertical line indicates the statistical significance of the effects (95% of confidence).
**Figure S6.** $^1$H (left panel) and $^{13}$C (right panel) NMR spectra in DMSO of the ionic surfactants synthesized: (A) [N$_{11112}$][C$_{12}$O$_2$]; (B) [N$_{11112}$][C$_{10}$O$_2$]; (C) [N$_{11112}$][C$_8$O$_2$]; (D) [N$_{11110}$][C$_{12}$O$_2$]; (E) [N$_{11110}$][C$_{10}$O$_2$]; (F) [N$_{11110}$][C$_8$O$_2$]; (G) [N$_{1118}$][C$_{12}$O$_2$]; (H) [N$_{1118}$][C$_{10}$O$_2$]; (I) [N$_{1118}$][C$_8$O$_2$].