# Supplementary Material

## Supported ionic liquids as efficient materials to remove non-steroidal anti-inflammatory drugs from aqueous media

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The adsorption efficiency (% AE) was determined according to Eq. S1:

$$\% AE = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100 \quad \text{(S1)}$$

**where $C_0$ is the initial concentration of sodium diclofenac in solution and Ce is the equilibrium concentration of sodium diclofenac after adsorption onto SILs ($mmol.L^{-1}$)**

**Table SI1.** Physicochemical properties of sodium diclofenac.[1, 2]

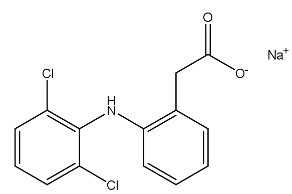
| **Properties** | |
|---|---|
| Chemical structure |  |
| Molecular formula | $C_{14}H_{10}Cl_2NNaO_2$ |
| Molecular weight | 318.129 g/mol |
| CAS | 15307-79-6 |
| Water solubility | 0.00482 mg/mL (25 °C) |
| Melting point | 283-285 °C |
| p$K_a$ | 4.0 |
| Log $K_{ow}$ | 4.75 |

**Table SI2.** Method used on the reusability tests of [Si][$C_3C_1$im]Cl.

| Adsorption | Treatment 1 | Desorption | Treatment 2 |
|---|---|---|---|
| 10 mL<br>Drug at 1.25 g/L<br>2h | 8 mL NaCl (0.5 M)<br>2 mL HCl (0.5 M) | 10 mL<br>1- BuOH:$H_2O$ (85:15, v:v)<br>2h | 2 mL<br>NaCl (0.5 M) |

**Table SI3.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im]Cl at 298 K.

| **[Si][$C_3C_1$im]Cl** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 61.8 ± 0.3 | 0.033 | 0.202 ± 0.008 |
| 2 | 73.8 ± 1.1 | 0.022 | 0.254 ± 0.002 |
| 3 | 75.8 ± 1.2 | 0.021 | 0.258 ± 0.014 |
| 4 | 75.9 ± 0.3 | 0.021 | 0.264 ± 0.004 |
| 5 | 79.2 ± 1.5 | 0.018 | 0.267 ± 0.003 |
| 6 | 86.2 ± 1.4 | 0.012 | 0.295 ± 0.014 |
| 7 | 81.0 ± 1.9 | 0.016 | 0.264 ± 0.001 |
| 8 | 86.9 ± 0.8 | 0.011 | 0.285 ± 0.002 |
| 9 | 86.3 ± 1.7 | 0.012 | 0.290 ± 0.018 |
| 10 | 90.7 ± 1.4 | 0.008 | 0.307 ± 0.013 |
| 15 | 90.1 ± 1.6 | 0.008 | 0.306 ± 0.002 |
| 30 | 91.5 ± 0.9 | 0.007 | 0.308 ± 0.011 |
| 45 | 92.3 ± 0.7 | 0.007 | 0.306 ± 0.014 |
| 60 | 92.1 ± 1.0 | 0.007 | 0.311 ± 0.003 |
| 120 | 92.2 ± 0.8 | 0.007 | 0.305 ± 0.015 |
| 180 | 92.9 ± 0.4 | 0.006 | 0.310 ± 0.001 |

**Table SI4.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im][SCN] at 298 K.

| **[Si][$C_3C_1$im][SCN]** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 64.4 ± 0.8 | 0.031 | 0.231 ± 0.008 |
| 2 | 71.6 ± 1.8 | 0.025 | 0.243 ± 0.021 |
| 3 | 74.1 ± 0.2 | 0.023 | 0.251 ± 0.014 |
| 4 | 75.9 ± 0.8 | 0.021 | 0.263 ± 0.019 |
| 5 | 76.0 ± 1.2 | 0.021 | 0.263 ± 0.026 |
| 6 | 76.7 ± 0.8 | 0.020 | 0.272 ± 0.015 |
| 7 | 79.2 ± 3.1 | 0.018 | 0.279 ± 0.013 |
| 8 | 81.3 ± 2.5 | 0.016 | 0.277 ± 0.004 |
| 9 | 79.9 ± 2.9 | 0.018 | 0.288 ± 0.007 |
| 10 | 81.9 ± 0.6 | 0.016 | 0.274 ± 0.023 |
| 15 | 81.0 ± 0.8 | 0.017 | 0.294 ± 0.015 |
| 30 | 82.9 ± 2.4 | 0.015 | 0.292 ± 0.021 |
| 45 | 83.3 ± 0.9 | 0.015 | 0.291 ± 0.005 |
| 60 | 83.0 ± 0.3 | 0.015 | 0.297 ± 0.008 |
| 120 | 83.4 ± 0.5 | 0.015 | 0.299 ± 0.011 |
| 180 | 82.9 ± 0.4 | 0.015 | 0.299 ± 0.008 |

**Table SI5.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im][N(CN)$_2$] at 298 K.

| **[Si][$C_3C_1$im][N(CN)$_2$]** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 70.3 ± 0.8 | 0.026 | 0.225 ± 0.01 |
| 2 | 75.2 ± 0.5 | 0.022 | 0.251 ± 0.007 |
| 3 | 77.0 ± 2.6 | 0.020 | 0.273 ± 0.011 |
| 4 | 79.1 ± 2.3 | 0.018 | 0.292 ± 0.001 |
| 5 | 78.7 ± 0.3 | 0.019 | 0.288 ± 0.010 |
| 6 | 80.3 ± 0.3 | 0.017 | 0.267 ± 0.010 |
| 7 | 82.0 ± 1.3 | 0.016 | 0.289 ± 0.017 |
| 8 | 82.7 ± 3.3 | 0.015 | 0.286 ± 0.017 |
| 9 | 86.5 ± 0.8 | 0.010 | 0.288 ± 0.006 |
| 10 | 85.7 ± 0.3 | 0.010 | 0.289 ± 0.004 |
| 15 | 87.9 ± 1.1 | 0.009 | 0.284 ± 0.004 |
| 30 | 88.5 ± 0.9 | 0.008 | 0.280 ± 0.003 |
| 45 | 89.1 ± 0.7 | 0.008 | 0.281 ± 0.003 |
| 60 | 88.5 ± 0.5 | 0.008 | 0.285 ± 0.020 |
| 120 | 88.8 ± 1.3 | 0.008 | 0.283 ± 0.008 |
| 180 | 87.8 ± 1.7 | 0.009 | 0.283 ± 0.004 |

**Table SI6.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im][Tos] at 298 K.

| **[Si][$C_3C_1$im][Tos]** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 63.4 ± 0.5 | 0.026 | 0.164 ± 0.005 |
| 2 | 67.1 ± 0.6 | 0.023 | 0.191 ± 0.001 |
| 3 | 74.9 ± 0.8 | 0.018 | 0.205 ± 0.013 |
| 4 | 73.2 ± 1.1 | 0.019 | 0.214 ± 0.009 |
| 5 | 72.5 ± 0.9 | 0.021 | 0.225 ± 0.004 |
| 6 | 74.7 ± 0.1 | 0.020 | 0.219 ± 0.016 |
| 7 | 76.4 ± 0.6 | 0.018 | 0.214 ± 0.009 |
| 8 | 77.2 ± 0.8 | 0.018 | 0.241 ± 0.011 |
| 9 | 77.0 ± 1.7 | 0.018 | 0.228 ± 0.008 |
| 10 | 74.9 ± 0.8 | 0.019 | 0.223 ± 0.005 |
| 15 | 74.9 ± 0.8 | 0.019 | 0.234 ± 0.009 |
| 30 | 76.8 ± 1.3 | 0.018 | 0.231 ± 0.014 |
| 45 | 76.8 ± 2.2 | 0.018 | 0.235 ± 0.008 |
| 60 | 76.7 ± 1.4 | 0.018 | 0.237 ± 0.008 |
| 120 | 76.5 ± 1.7 | 0.018 | 0.234 ± 0.016 |
| 180 | 77.4 ± 1.4 | 0.017 | 0.230 ± 0.013 |

**Table SI7.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im][Male] at 298 K.

| **[Si][$C_3C_1$im][Male]** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 57.5 ± 1.1 | 0.033 | 0.174 ± 0.015 |
| 2 | 60.7 ± 0.1 | 0.030 | 0.182 ± 0.004 |
| 3 | 62.6 ± 2.8 | 0.029 | 0.195 ± 0.001 |
| 4 | 64.9 ± 0.6 | 0.027 | 0.201 ± 0.012 |
| 5 | 63.2 ± 1.1 | 0.028 | 0.196 ± 0.007 |
| 6 | 66.5 ± 1.3 | 0.026 | 0.200 ± 0.024 |
| 7 | 65.5 ± 2.2 | 0.027 | 0.199 ± 0.014 |
| 8 | 67.2 ± 0.8 | 0.025 | 0.198 ± 0.007 |
| 9 | 67.9 ± 0.5 | 0.025 | 0.215 ± 0.015 |
| 10 | 68.4 ± 0.5 | 0.024 | 0.207 ± 0.007 |
| 15 | 68.5 ± 0.2 | 0.024 | 0.203 ± 0.016 |
| 30 | 69.3 ± 0.8 | 0.024 | 0.205 ± 0.014 |
| 45 | 68.8 ± 0.2 | 0.024 | 0.201 ± 0.013 |
| 60 | 69.3 ± 0.1 | 0.024 | 0.201 ± 0.005 |
| 120 | 68.7 ± 0.9 | 0.024 | 0.210 ± 0.003 |
| 180 | 68.4 ± 1.0 | 0.024 | 0.211 ± 0.002 |

**Table SI8.** Adsorption efficiency (%AE), equilibrium concentration after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), using [Si][$C_3C_1$im][$NTf_2$] at 298 K.

| **[Si][$C_3C_1$im][$NTf_2$]** | | | |
|---|---|---|---|
| **t / min** | **% (AE ± σ)** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 1 | 44.2 ± 1.2 | 0.040 | 0.116 ± 0.006 |
| 2 | 44.6 ± 0.3 | 0.040 | 0.119 ± 0.011 |
| 3 | 47.0 ± 1.2 | 0.038 | 0.129 ± 0.003 |
| 4 | 52.8 ± 2.6 | 0.034 | 0.154 ± 0.004 |
| 5 | 56.4 ± 0.7 | 0.031 | 0.158 ± 0.002 |
| 6 | 56.9 ± 0.7 | 0.031 | 0.172 ± 0.001 |
| 7 | 63.1 ± 2.4 | 0.027 | 0.173 ± 0.003 |
| 8 | 67.7 ± 0.5 | 0.023 | 0.184 ± 0.013 |
| 9 | 68.2 ± 0.2 | 0.023 | 0.179 ± 0.005 |
| 10 | 68.9 ± 0.3 | 0.022 | 0.192 ± 0.010 |
| 15 | 70.4 ± 0.9 | 0.021 | 0.193 ± 0.016 |
| 30 | 73.1 ± 0.4 | 0.019 | 0.204 ± 0.011 |
| 45 | 73.8 ± 0.2 | 0.019 | 0.204 ± 0.016 |
| 60 | 73.3 ± 0.9 | 0.019 | 0.212 ± 0.006 |
| 120 | 73.3 ± 0.1 | 0.019 | 0.217 ± 0.014 |
| 180 | 72.3 ± 1.0 | 0.020 | 0.217 ± 0.001 |

**Table SI9.** Equilibrium concentration of diclofenac after adsorption ($C_e$), concentration of adsorbate in the solid phase ($q_e$), and respective standard deviations (σ), at 298 K.

| **[Si][$C_3C_1$im]Cl** | | **[Si][$C_3C_1$im][SCN]** | | **[Si][$C_3C_1$im[N(CN)$_2$]** | |
|---|---|---|---|---|---|
| **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** | **$C_e$ / mmol.L$^{-1}$** | **($q_e$ ± σ) / mmol.g$^{-1}$** |
| 0.000 | 0.000 ± 0.000 | 0.000 | 0.000 ± 0.000 | 0.000 | 0.000 ± 0.000 |
| 0.002 | 0.031 ± 0.003 | 0.001 | 0.010 ± 0.000 | 0.001 | 0.010 ± 0.000 |
| 0.006 | 0.270 ± 0.012 | 0.004 | 0.113 ± 0.006 | 0.002 | 0.112 ± 0.004 |
| 0.006 | 0.168 ± 0.001 | 0.006 | 0.173 ± 0.001 | 0.005 | 0.167 ± 0.001 |
| 0.007 | 0.283 ± 0.000 | 0.01 | 0.266 ± 0.012 | 0.006 | 0.287 ± 0.013 |
| 0.012 | 0.547 ± 0.000 | 0.015 | 0.293 ± 0.002 | 0.011 | 0.324 ± 0.003 |
| 0.015 | 0.308 ± 0.001 | 0.026 | 0.371 ± 0.008 | 0.026 | 0.391 ± 0.006 |
| 0.026 | 0.358 ± 0.005 | 0.036 | 0.439 ± 0.025 | 0.036 | 0.424 ± 0.013 |
| 0.036 | 0.439 ± 0.023 | 0.046 | 0.422 ± 0.011 | 0.045 | 0.436 ± 0.004 |
| 0.073 | 0.651 ± 0.016 | 0.065 | 0.344 ± 0.003 | 0.056 | 0.398 ± 0.004 |
| 0.097 | 0.605 ± 0.028 | 0.118 | 0.460 ± 0.016 | 0.114 | 0.475 ± 0.006 |
| 0.226 | 0.695 ± 0.037 | 0.249 | 0.476 ± 0.052 | 0.236 | 0.483 ± 0.039 |
| 0.236 | 0.644 ± 0.003 | 0.299 | 0.514 ± 0.029 | 0.306 | 0.549 ± 0.031 |
| 0.399 | 0.722 ± 0.071 | 0.45 | 0.468 ± 0.064 | 0.433 | 0.486 ± 0.042 |
| 0.551 | 0.743 ± 0.061 | 0.507 | 0.490 ± 0.039 | 0.512 | 0.501 ± 0.019 |
| 0.610 | 0.736 ± 0.029 | 0.783 | 0.504 ± 0.001 | 0.786 | 0.529 ± 0.029 |
| 0.980 | 0.748 ± 0.068 | 0.882 | 0.509 ± 0.031 | 0.873 | 0.570 ± 0.024 |
| 1.314 | 0.733 ± 0.047 | 1.336 | 0.538 ± 0.067 | 1.322 | 0.585 ± 0.005 |
| 1.371 | 0.758 ± 0.010 | 1.421 | 0.519 ± 0.013 | 1.424 | 0.547 ± 0.040 |
| **[Si][$C_3C_1$im][Tos]** | | **[Si][$C_3C_1$im][Male]** | | **[Si][$C_3C_1$im][NTf$_2$]** | |
| **$C_e$ / mmol.L$^{-1}$** | **$q_e$ ± σ / mmol.g$^{-1}$** | **$C_e$ / mmol.L$^{-1}$** | **$q_e$ ± σ / mmol.g$^{-1}$** | **$C_e$ / mmol.L$^{-1}$** | **$q_e$ ± σ / mmol.g$^{-1}$** |
| 0.000 | 0.000 ± 0.000 | 0.000 | 0.000 ± 0.000 | 0.000 | 0.000 ± 0.000 |
| 0.003 | 0.004 ± 0.001 | 0.003 | 0.002 ± 0.001 | 0.001 | 0.012 ± 0.002 |
| 0.004 | 0.110 ± 0.000 | 0.011 | 0.082 ± 0.004 | 0.006 | 0.116 ± 0.009 |
| 0.009 | 0.292 ± 0.002 | 0.019 | 0.148 ± 0.005 | 0.009 | 0.136 ± 0.000 |
| 0.011 | 0.145 ± 0.001 | 0.022 | 0.229 ± 0.002 | 0.024 | 0.225 ± 0.005 |
| 0.019 | 0.278 ± 0.024 | 0.026 | 0.264 ± 0.023 | 0.031 | 0.308 ± 0.000 |
| 0.033 | 0.316 ± 0.008 | 0.035 | 0.326 ± 0.034 | 0.043 | 0.300 ± 0.000 |
| 0.043 | 0.390 ± 0.007 | 0.052 | 0.403 ± 0.023 | 0.047 | 0.343 ± 0.010 |
| 0.049 | 0.375 ± 0.021 | 0.105 | 0.535 ± 0.004 | 0.056 | 0.323 ± 0.008 |
| 0.058 | 0.373 ± 0.009 | 0.209 | 0.554 ± 0.002 | 0.122 | 0.414 ± 0.055 |
| 0.127 | 0.464 ± 0.009 | 0.275 | 0.654 ± 0.045 | 0.220 | 0.439 ± 0.022 |
| 0.245 | 0.471 ± 0.046 | 0.382 | 0.671 ± 0.053 | 0.302 | 0.446 ± 0.047 |
| 0.305 | 0.516 ± 0.027 | 0.453 | 0.684 ± 0.042 | 0.372 | 0.532 ± 0.034 |
| 0.439 | 0.474 ± 0.006 | 0.732 | 0.742 ± 0.035 | 0.468 | 0.544 ± 0.077 |
| 0.513 | 0.505 ± 0.002 | 0.831 | 0.778 ± 0.057 | 0.666 | 0.652 ± 0.048 |
| 0.793 | 0.491 ± 0.034 | 1.132 | 0.922 ± 0.015 | 0.820 | 0.695 ± 0.065 |
| 0.875 | 0.529 ± 0.056 | 1.228 | 0.967 ± 0.036 | 1.169 | 0.767 ± 0.095 |
| 1.335 | 0.537 ± 0.065 | 1.244 | 0.951 ± 0.041 | | |
| 1.421 | 0.546 ± 0.047 | 1.321 | 0.979 ± 0.027 | | |

**Table SI10.** Sodium diclofenac desorption efficiency from [Si][$C_3C_1$im]Cl with several solvents and respective standard deviations (σ) at 298 K.

| **Solvent** | **Desorption Efficiency ± σ** |
|---|---|
| Metanol | 24.7 ± 3.2 |
| Ethanol | 28.8 ± 2.1 |
| 1-butanol | 33.0 ± 3.9 |
| 2-butanol | 26.3 ± 1.3 |
| 1-butanol:water (85:15, v:v) | 61.2 ± 8.7 |
| 2-butanol: water (85:15, v:v) | 42.5 ± 5.4 |
| water | 10.1 ± 0.9 |

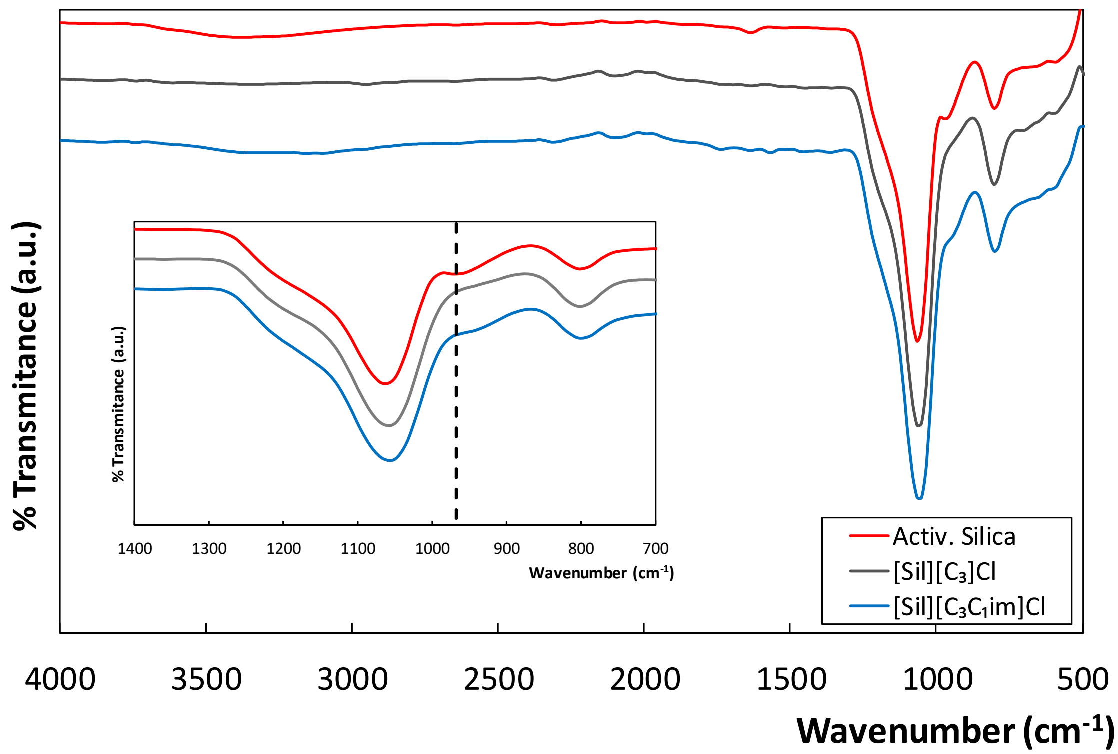



**Fig. SI1.** FTIR spectra of activated silica (red line), chloropropyl silica (green line), and supported *N*-methylimidazolium-based ionic liquid (blue line).

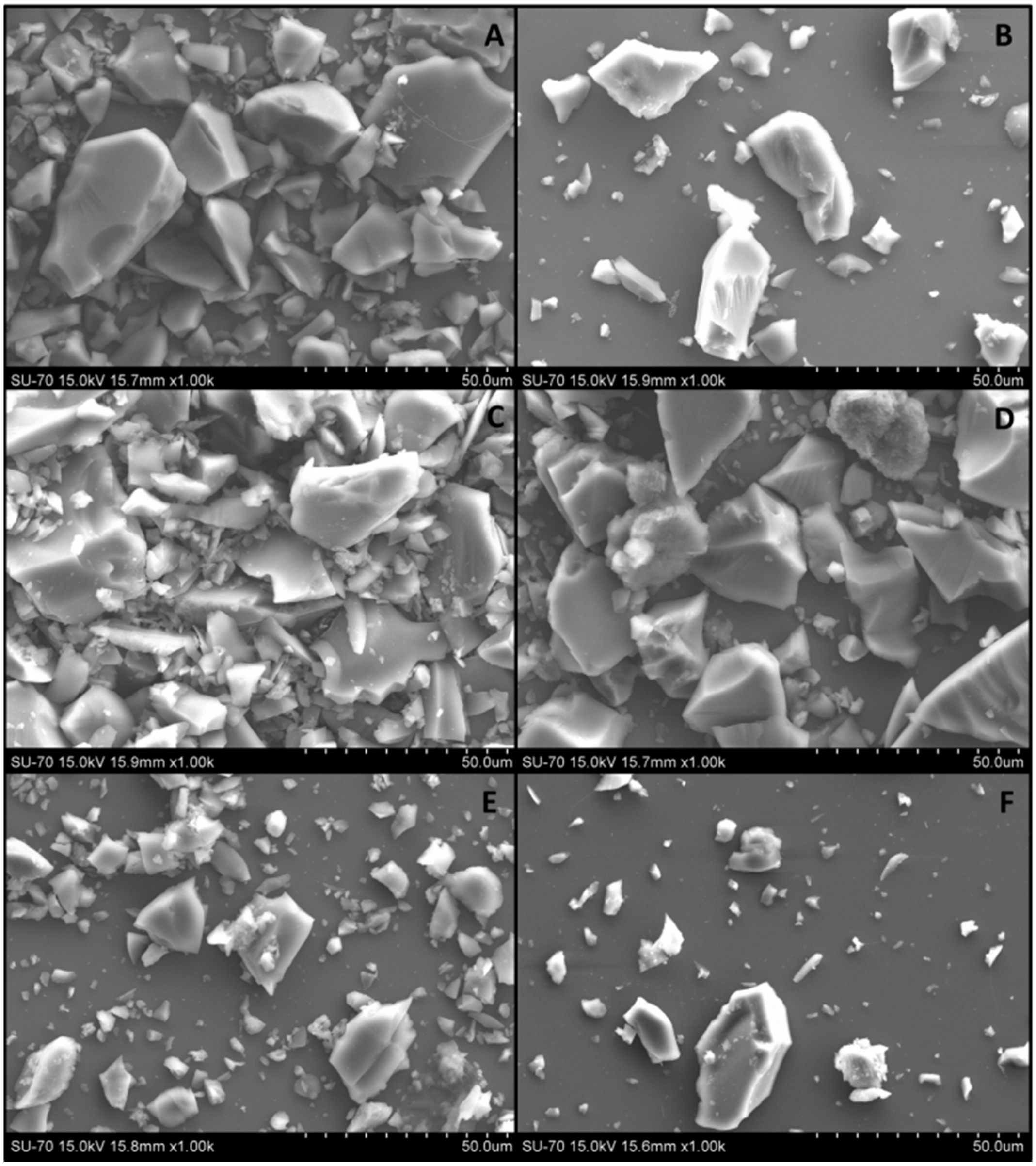



**Fig. SI2.** Scanning electron microscope images of: A) [Si][$C_3C_1$im]Cl; B) [Si][$C_3C_1$im][SCN]; C) [Si][$C_3C_1$im][$N(CN)_2$]; D) [Si][$C_3C_1$im][Tos]; E) [Si][$C_3C_1$im][Male]; and F) [Si][$C_3C_1$im][$NTf_2$].

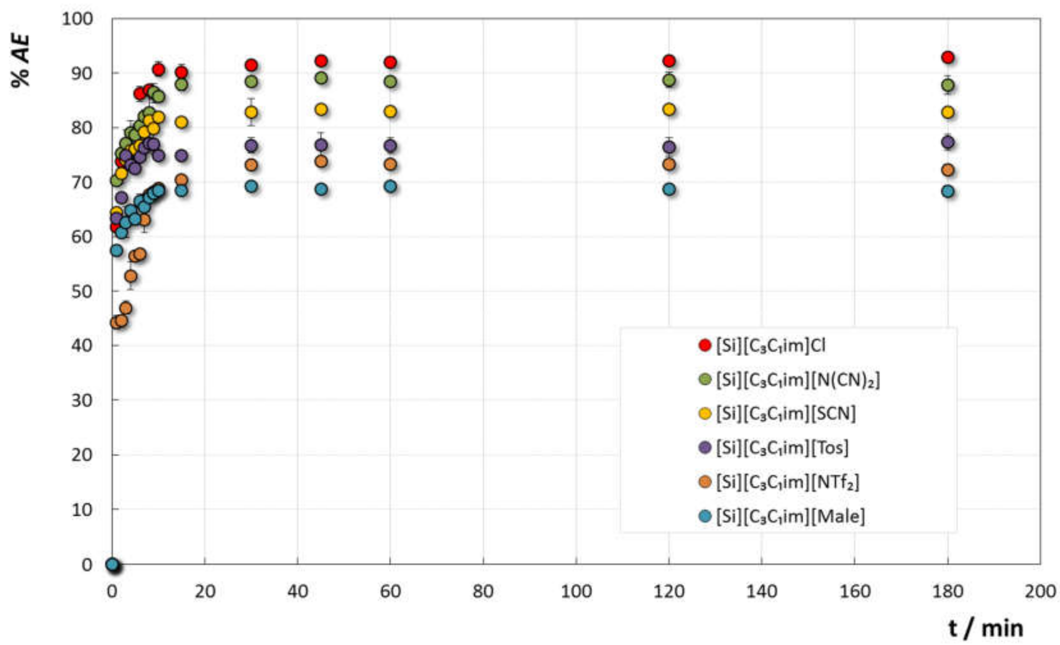



**Fig. SI3.** Adsorption efficiency of the six studied SILPs for sodium diclofenac at 298 K: ●, [Si][$C_3C_1$im]Cl; ●, [Si][$C_3C_1$im][SCN]; ●, [Si][$C_3C_1$im[N(CN)$_2$]; ●, [Si][$C_3C_1$im][Tos]; ●, [Si][$C_3C_1$im][Male]; and ●, [Si][$C_3C_1$im][NTf$_2$].

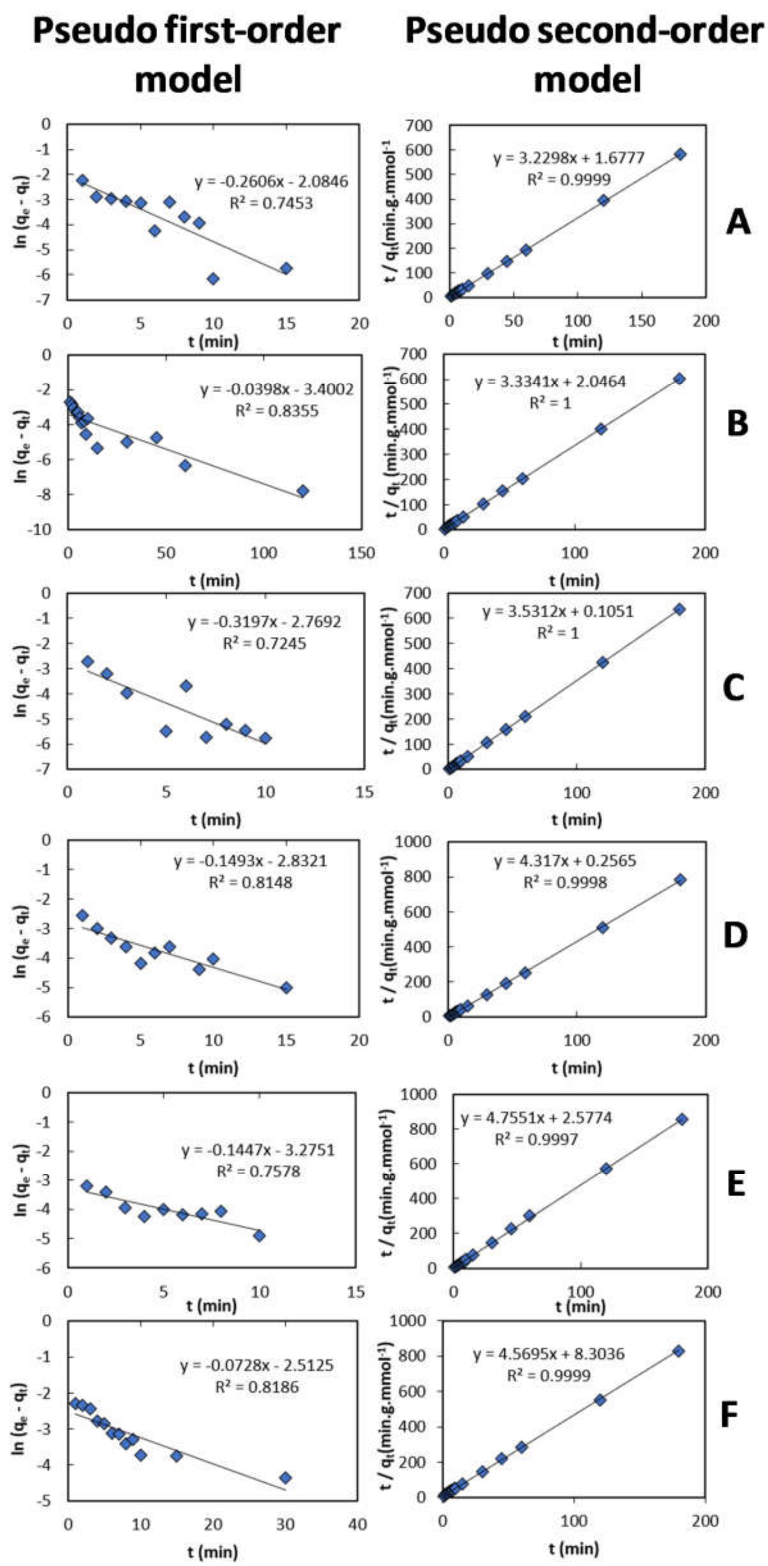



**Fig. SI4.** Fitting by the pseudo first-order and pseudo second-order kinetic models using: A) [Si][$C_3C_1$im]Cl; B) [Si][$C_3C_1$im][SCN]; C) [Si][$C_3C_1$im[N(CN)$_2$]; D) [Si][$C_3C_1$im][Tos]; E) [Si][$C_3C_1$im][Male]; and F) [Si][$C_3C_1$im][NTf$_2$].

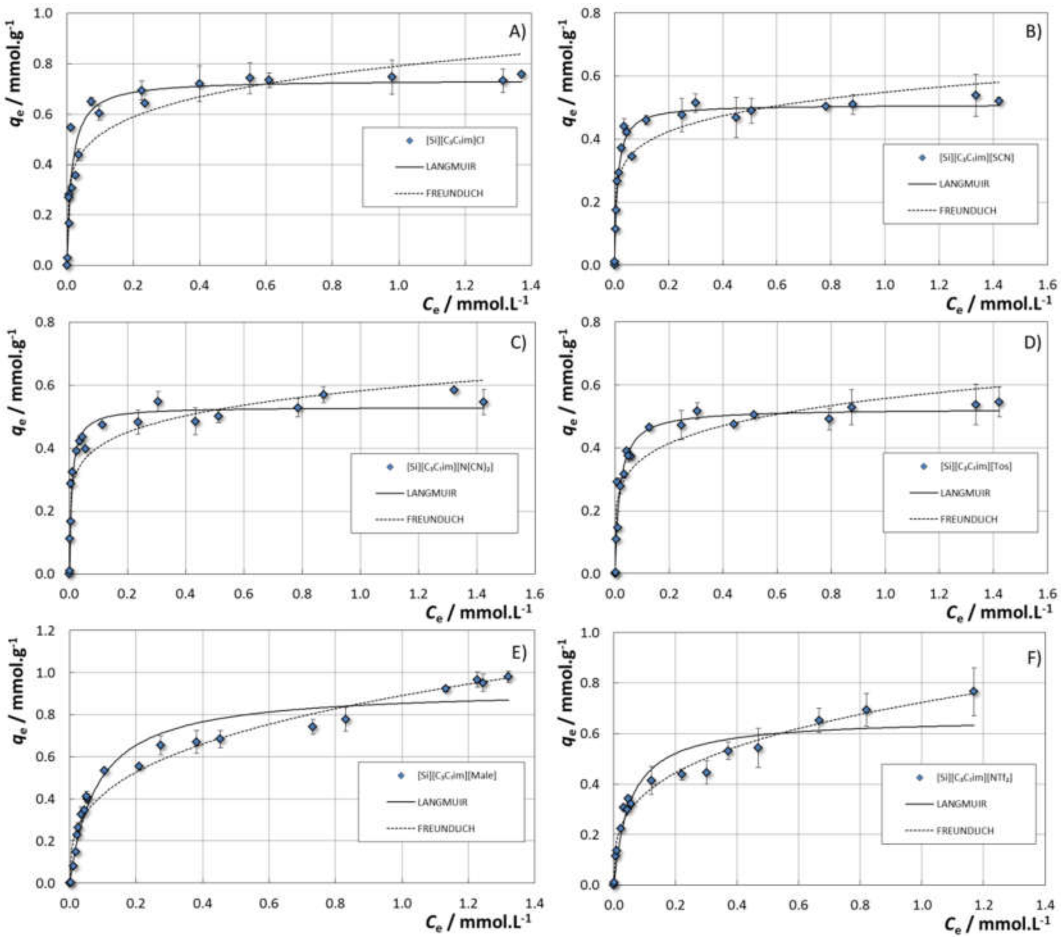



**Fig. SI5.** Adsorption isotherms of sodium diclofenac in SILPs at 25 ºC: ◆, experimental data; solid lines, Langmuir model; and dotted lines, Freundlich model.

## References


1. ChemSpider - The free chemical database at www.chemspider.com (Accessed January 2019).
2. Drug Bank - Open Data Drug & Drug Target Database at http://www.drugbank.ca (Accessed January 2019).