

Electronic Supplementary Information

Risk assessment of trace metals in sunblock creams using DABCONium-based ionic liquid functionalized magnetic nanoparticles

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Table S1. The applied values of the chosen factors of CCD.

| Factors | Name | Units | Level | | | | |
|----------|-----------------|---------------|-------------|-----|------|-----|-----------|
| | | | $-\alpha^a$ | -1 | 0 | 1 | $+\alpha$ |
| A | Sample pH | | 1 | 3 | 5 | 7 | 9 |
| B | Sorbent dosage | mg | 7.5 | 10 | 12.5 | 15 | 17.5 |
| C | Extraction time | min | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| D | Desorption time | min | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| E | Eluent amount | μL | 50 | 300 | 550 | 800 | 1050 |
| Response | ER | % | | | | | |

^a $\alpha = 2.0$.

Table S2. Results of the CCD.

| Run | Factors ^a | | | | | Response ^b | | | |
|-----|----------------------|----|----|----|----|-----------------------|--------|-------|-------|
| | A | B | C | D | E | Cd | Cr | Ni | Pb |
| 1 | 0 | 0 | 2 | 0 | 0 | 95.86 | 97.23 | 96.07 | 93.95 |
| 2 | 1 | -1 | -1 | 1 | 1 | 48.74 | 50.97 | 48.65 | 47.39 |
| 3 | -1 | 1 | -1 | -1 | -1 | 66.29 | 65.41 | 65.15 | 64.23 |
| 4 | 0 | -2 | 0 | 0 | 0 | 77.23 | 77.75 | 76.97 | 76.53 |
| 5 | 1 | 1 | 1 | 1 | 1 | 51.32 | 51.45 | 50.78 | 48.59 |
| 6 | 1 | -1 | -1 | -1 | -1 | 71.31 | 70.54 | 67.45 | 65.99 |
| 7 | 0 | 0 | 0 | 0 | 2 | 65.36 | 69.15 | 65.36 | 64.45 |
| 8 | 1 | 1 | -1 | -1 | 1 | 63.49 | 67.26 | 65.46 | 64.06 |
| 9 | 0 | 0 | 0 | 0 | 0 | 99.15 | 98.78 | 96.45 | 95.35 |
| 10 | -1 | -1 | 1 | -1 | -1 | 74.53 | 76.35 | 74.87 | 75.15 |
| 11 | -1 | 1 | 1 | 1 | -1 | 77.95 | 77.69 | 77.09 | 76.54 |
| 12 | -1 | -1 | 1 | 1 | 1 | 68.19 | 72.36 | 72.15 | 66.34 |
| 13 | -2 | 0 | 0 | 0 | 0 | 86.04 | 86.72 | 86.07 | 86.92 |
| 14 | -1 | -1 | -1 | -1 | 1 | 64.59 | 67.32 | 69.42 | 61.85 |
| 15 | 1 | -1 | 1 | -1 | 1 | 73.64 | 71.18 | 70.14 | 68.81 |
| 16 | 0 | 0 | 0 | 0 | 0 | 98.45 | 99.74 | 96.36 | 94.62 |
| 17 | -1 | -1 | -1 | 1 | -1 | 71.7 | 72.63 | 70.88 | 69.56 |
| 18 | 1 | 1 | -1 | 1 | -1 | 47.09 | 50.65 | 49.57 | 44.97 |
| 19 | -1 | 1 | 1 | -1 | 1 | 80.15 | 82.64 | 80.02 | 78.56 |
| 20 | 0 | 0 | -2 | 0 | 0 | 75.38 | 76.77 | 76.23 | 76.34 |
| 21 | 1 | 1 | 1 | -1 | -1 | 59.45 | 59.47 | 60.65 | 59.38 |
| 22 | 0 | 0 | 0 | 2 | 0 | 58.77 | 58.47 | 57.85 | 58.12 |
| 23 | 0 | 0 | 0 | 0 | 0 | 96.24 | 98.35 | 96.86 | 97.15 |
| 24 | 0 | 0 | 0 | 0 | 0 | 96.56 | 100.17 | 97.65 | 96.45 |
| 25 | 0 | 0 | 0 | -2 | 0 | 65.42 | 66.45 | 65.15 | 64.07 |
| 26 | 0 | 0 | 0 | 0 | -2 | 70.61 | 71.13 | 70.65 | 69.99 |
| 27 | 0 | 2 | 0 | 0 | 0 | 70.15 | 71.69 | 69.41 | 67.92 |
| 28 | -1 | 1 | -1 | 1 | 1 | 71.59 | 72.45 | 71.63 | 71.15 |
| 29 | 0 | 0 | 0 | 0 | 0 | 98.62 | 97.15 | 98.72 | 96.34 |
| 30 | 2 | 0 | 0 | 0 | 0 | 63.07 | 61.18 | 62.49 | 62.04 |
| 31 | 0 | 0 | 0 | 0 | 0 | 96.56 | 100.61 | 97.15 | 94.63 |
| 32 | 1 | -1 | 1 | 1 | -1 | 76.46 | 80.14 | 78.52 | 77.42 |

^a A: Sample pH, B: Sorbent dosage (mg), C: Extraction time (min), D: Desorption time (min), E: Eluent amount (μL)

^b Extraction recovery (%)

Table S3. ANOVA table for quadratic model (Response: Mean ER%).

| Source | Cd | | | Cr | | | Ni | | | Pb | | |
|--------------------------------|-------------|---------|----------|-------------|---------|----------|-------------|---------|----------|-------------|---------|----------|
| | Mean Square | F-value | p-value | Mean Square | F-value | p-value | Mean Square | F-value | p-value | Mean Square | F-value | p-value |
| Model | 346.87 | 141.13 | < 0.0001 | 350.89 | 104.84 | < 0.0001 | 335.33 | 204.7 | < 0.0001 | 348.75 | 181.08 | < 0.0001 |
| A | 698.01 | 283.99 | < 0.0001 | 773.73 | 231.17 | < 0.0001 | 783.76 | 478.43 | < 0.0001 | 776.69 | 403.27 | < 0.0001 |
| B | 88.13 | 35.86 | < 0.0001 | 90.44 | 27.02 | 0.0003 | 91.46 | 55.83 | < 0.0001 | 74.38 | 38.62 | < 0.0001 |
| C | 398.94 | 162.31 | < 0.0001 | 375.8 | 112.28 | < 0.0001 | 381.52 | 232.9 | < 0.0001 | 390.51 | 202.76 | < 0.0001 |
| D | 120.2 | 48.9 | < 0.0001 | 95.16 | 28.43 | 0.0002 | 97.97 | 59.8 | < 0.0001 | 95.88 | 49.78 | < 0.0001 |
| E | 46.96 | 19.1 | 0.0011 | 18.74 | 5.6 | 0.0374 | 29.28 | 17.88 | 0.0014 | 58.81 | 30.54 | 0.0002 |
| AB | 270.36 | 110 | < 0.0001 | 179.09 | 53.51 | < 0.0001 | 125.83 | 76.81 | < 0.0001 | 226.43 | 117.57 | < 0.0001 |
| AC | 0.8055 | 0.3277 | 0.5785 | 4.42 | 1.32 | 0.2748 | 0.228 | 0.1392 | 0.7162 | 0.2475 | 0.1285 | 0.7268 |
| AD | 144.9 | 58.95 | < 0.0001 | 93.36 | 27.89 | 0.0003 | 92.5 | 56.46 | < 0.0001 | 119.19 | 61.89 | < 0.0001 |
| AE | 7.8 | 3.17 | 0.1025 | 32.01 | 9.56 | 0.0102 | 43.53 | 26.57 | 0.0003 | 8.02 | 4.17 | 0.066 |
| BC | 16.14 | 6.57 | 0.0264 | 33.32 | 9.96 | 0.0092 | 31.78 | 19.4 | 0.0011 | 36.81 | 19.11 | 0.0011 |
| BD | 0.3752 | 0.1526 | 0.7035 | 10.97 | 3.28 | 0.0976 | 6.93 | 4.23 | 0.0642 | 12.06 | 6.26 | 0.0294 |
| BE | 186.39 | 75.83 | < 0.0001 | 213.23 | 63.71 | < 0.0001 | 136.83 | 83.53 | < 0.0001 | 232.33 | 120.63 | < 0.0001 |
| CD | 10.1 | 4.11 | 0.0676 | 15.66 | 4.68 | 0.0534 | 24.03 | 14.67 | 0.0028 | 6.31 | 3.28 | 0.0976 |
| CE | 3.16 | 1.29 | 0.281 | 13.67 | 4.08 | 0.0683 | 25.38 | 15.49 | 0.0023 | 41.89 | 21.75 | 0.0007 |
| DE | 119.08 | 48.45 | < 0.0001 | 159.45 | 47.64 | < 0.0001 | 154.82 | 94.5 | < 0.0001 | 118.54 | 61.55 | < 0.0001 |
| A ² | 969.14 | 394.3 | < 0.0001 | 1113.03 | 332.54 | < 0.0001 | 929.93 | 567.66 | < 0.0001 | 893.69 | 464.02 | < 0.0001 |
| B ² | 1043.44 | 424.53 | < 0.0001 | 1044.55 | 312.08 | < 0.0001 | 1022.12 | 623.94 | < 0.0001 | 1085.56 | 563.65 | < 0.0001 |
| C ² | 260.79 | 106.1 | < 0.0001 | 246.25 | 73.57 | < 0.0001 | 208.01 | 126.98 | < 0.0001 | 238.83 | 124.01 | < 0.0001 |
| D ² | 2304.19 | 937.48 | < 0.0001 | 2393.13 | 714.99 | < 0.0001 | 2284.73 | 1394.68 | < 0.0001 | 2305.73 | 1197.19 | < 0.0001 |
| E ² | 1602.15 | 651.85 | < 0.0001 | 1483.86 | 443.33 | < 0.0001 | 1520.3 | 928.05 | < 0.0001 | 1578.05 | 819.36 | < 0.0001 |
| Lack of Fit | 3.14 | 1.92 | 0.2452 | 4.75 | 2.87 | 0.134 | 2.35 | 3.02 | 0.123 | 2.62 | 2.38 | 0.1795 |
| R² | | | 0.9961 | | | 0.9948 | | | 0.9973 | | | 0.997 |
| Adjusted R² | | | 0.9891 | | | 0.9853 | | | 0.9924 | | | 0.9915 |
| Predicted R² | | | 0.9257 | | | 0.8913 | | | 0.9436 | | | 0.9417 |
| Adeq Precision | | | 40.0711 | | | 33.3771 | | | 47.4678 | | | 45.5127 |

Table S4. The effect of potentially interfering ions on the extraction recovery of the selected TMs
(n = 3).

| Ions | Interference to metal ion ratio | R% ^a ± S ^b | | | |
|-------------------------------|---------------------------------|----------------------------------|--------|--------|--------|
| | | Cd | Cr | Ni | Pb |
| Na ⁺ | 2500 | 97 ± 1 | 95 ± 2 | 96 ± 2 | 94 ± 2 |
| K ⁺ | 2000 | 95 ± 2 | 94 ± 2 | 97 ± 1 | 95 ± 2 |
| Mg ²⁺ | 1000 | 96 ± 1 | 95 ± 2 | 96 ± 1 | 94 ± 2 |
| Ca ²⁺ | 500 | 99 ± 2 | 96 ± 1 | 97 ± 2 | 95 ± 1 |
| Cu ²⁺ | 15 | 94 ± 2 | 92 ± 2 | 92 ± 2 | 93 ± 2 |
| Fe ³⁺ | 25 | 93 ± 2 | 91 ± 2 | 91 ± 3 | 89 ± 3 |
| Zn ²⁺ | 30 | 94 ± 3 | 92 ± 3 | 90 ± 1 | 92 ± 2 |
| Hg ²⁺ | 30 | 93 ± 2 | 92 ± 2 | 90 ± 1 | 91 ± 3 |
| As ³⁺ | 30 | 95 ± 2 | 93 ± 2 | 92 ± 2 | 92 ± 3 |
| Cl ⁻ | 2500 | 96 ± 1 | 97 ± 3 | 94 ± 3 | 94 ± 1 |
| PO ₄ ³⁻ | 2000 | 96 ± 2 | 95 ± 2 | 96 ± 1 | 93 ± 2 |
| SO ₄ ²⁻ | 1000 | 97 ± 1 | 95 ± 2 | 95 ± 2 | 94 ± 2 |
| CO ₃ ²⁻ | 2500 | 98 ± 1 | 96 ± 2 | 92 ± 3 | 92 ± 2 |

a Recovery

b Standard deviation

Table S5. Evaluation of the accuracy of the proposed using standard reference material (n=5).

| Certified values (mg kg ⁻¹) | | | Measured (mg kg ⁻¹) ^a | | | Recovery (%) | | | t _{exp} ^b | | |
|---|---------------|---------------|--|---------------|---------------|--------------|-------|-------|-------------------------------|-------|-------|
| Cd | Ni | Pb | Cd | Ni | Pb | Cd | Ni | Pb | Cd | Ni | Pb |
| 0.0132 ± 0.0015 | 0.936 ± 0.094 | 0.470 ± 0.024 | 0.0134 ± 0.0022 | 0.933 ± 0.128 | 0.464 ± 0.029 | 101.51 | 99.67 | 98.72 | 2.033 | - | -0.46 |
| | | | | | | | | | | 0.052 | |

^a The mean value ± SD based on five replicate determinations.

^b $t_{exp} = \frac{|\bar{x} - u|}{S/\sqrt{n}}$, where t_{exp} was statistical value (for four degrees of freedom, the critical value of t at the 95% confidence level is 2.132), μ was the reported values, x was the experimental mean value, n was the number of independent determinations, and S was the standard deviation.

Table S6. Validation experiment results without the pre-concentration method.

| Element | LOD ($\mu\text{g kg}^{-1}$) | LOQ ($\mu\text{g kg}^{-1}$) | Linear range ($\mu\text{g kg}^{-1}$) | (R^2) | Intra-day accuracy and precision (n=5) ^a | | | Inter-day accuracy and precision (n=15) | | |
|---------|----------------------------------|----------------------------------|---|---------|--|----------|-----------|--|----------|-----------|
| | | | | | RSD (%) | | | Recovery (%) | | |
| | | | | | Level I | Level II | Level III | Level I | Level II | Level III |
| Cd | 4.92 | 16.43 | 17-250 | 0.9914 | 5.94 | 5.21 | 4.65 | 79.67 | 83.45 | 84.45 |
| Cr | 9.16 | 30.56 | 31-300 | 0.9934 | 5.43 | 5.16 | 5.07 | 83.44 | 81.45 | 80.12 |
| Ni | 11.33 | 37.78 | 38-550 | 0.9975 | 5.13 | 4.97 | 4.49 | 78.42 | 79.65 | 82.32 |
| Pb | 27.62 | 92.08 | 93-550 | 0.9981 | 5.57 | 5.14 | 4.87 | 77.78 | 80.14 | 81.45 |

^a Level 1: LOQ, Level 2: 150 $\mu\text{g kg}^{-1}$, Level 3: 250 $\mu\text{g kg}^{-1}$ for Cd, 300 $\mu\text{g kg}^{-1}$ for Cr, 550 $\mu\text{g kg}^{-1}$ for Ni and Pb.

Table S7. Margin of Safety (MoS) for selected TMs in the sunblock products.

| Brand | Cd | Cr | Ni | Pb |
|-------------------------------|-----------|-----------|-----------|-----------|
| 50% bio-accessibility | | | | |
| A | 1830.86 | 823.07 | 1856.98 | 360.49 |
| B | 1019.72 | 2061.18 | 4659.89 | 448.09 |
| C | 1385.94 | 1985.00 | 2965.10 | 462.56 |
| D | 1348.25 | 1669.59 | 3613.48 | 419.64 |
| E | 886.47 | 1269.46 | 3555.66 | 402.04 |
| F | 1220.57 | 1170.33 | 3014.33 | 395.07 |
| G | 1013.31 | 1383.96 | 3556.64 | 448.09 |
| H | 1323.33 | 956.65 | 2414.63 | 347.19 |
| I | 1246.54 | 1113.70 | 4435.40 | 374.31 |
| J | 1889.92 | 1414.33 | 3273.05 | 429.93 |
| K | 1365.39 | 1105.43 | 2718.11 | 387.82 |
| 100% bio-accessibility | | | | |
| A | 1068.01 | 411.53 | 928.49 | 180.24 |
| B | 594.84 | 1030.59 | 2329.95 | 224.04 |
| C | 808.47 | 992.50 | 1482.55 | 231.28 |
| D | 786.48 | 834.80 | 1806.74 | 209.82 |
| E | 517.11 | 634.73 | 1777.83 | 201.02 |
| F | 712.00 | 585.17 | 1507.16 | 197.54 |
| G | 591.10 | 691.98 | 1778.32 | 224.04 |
| H | 771.94 | 478.33 | 1207.31 | 173.59 |
| I | 727.15 | 556.85 | 2217.70 | 187.15 |
| J | 1102.45 | 707.17 | 1636.52 | 214.96 |
| K | 796.48 | 644.83 | 1585.56 | 226.23 |

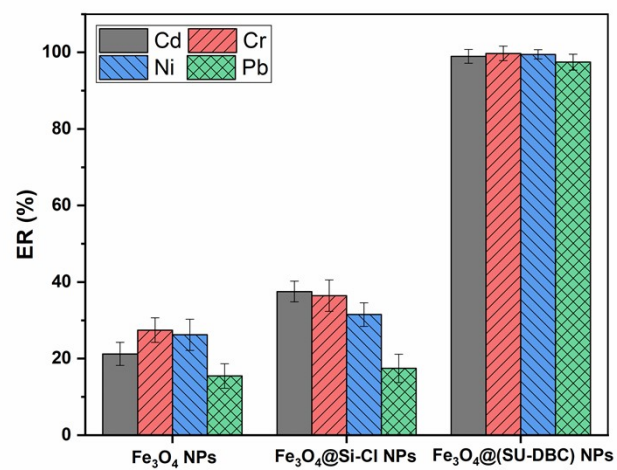


Fig. S1. a) Effect of type of nano-sorbent on ER.

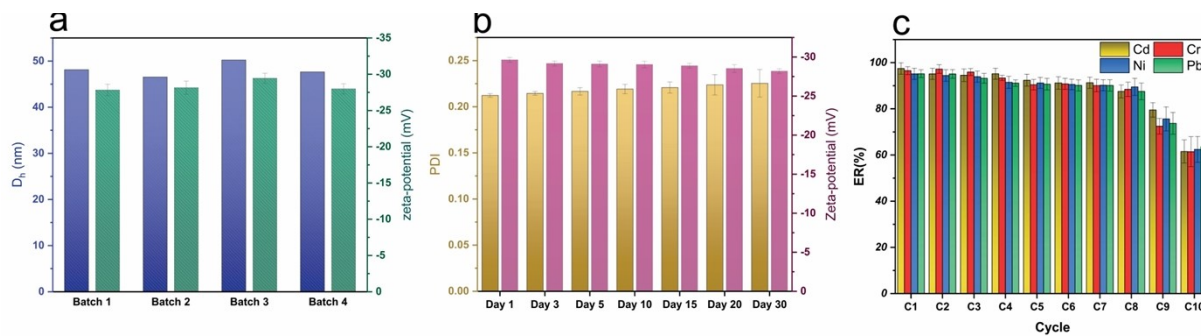
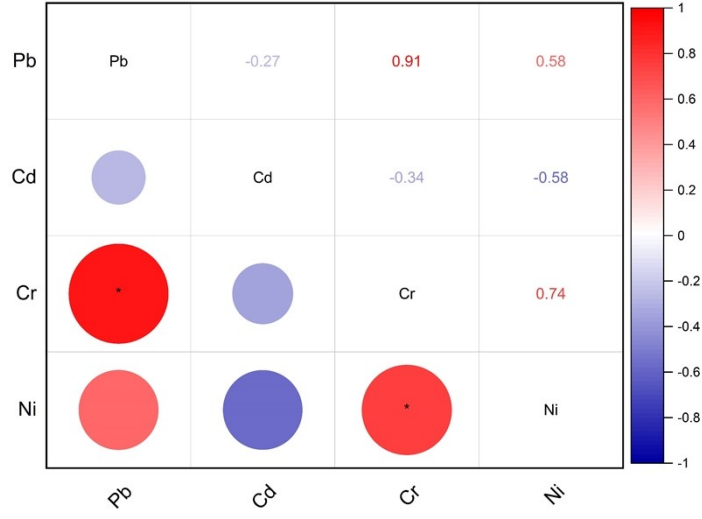


Fig. S2. a) Batch-to-batch reproducibility study of Fe₃O₄@(SU-DBC) NPs, **b)** Stability study of Fe₃O₄@(SU-DBC) NPs, **c)** Reusability of sorbent.



* p<=0.05

Fig. S3. Correlation coefficient of TMs' concentration (mg kg⁻¹) in sunblock products.