

Supplementary material

Alcohol-based deep eutectic solvents with pH-responsive hydrophobicity for the analysis of herbicides in water and food

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Table S1 The values of variables (volume of DES (A), concentration of KOH (B), and volume of HCl (C)) produced by the CCD experiments and the extraction recovery for Ala, Atz, and Met.

| No. | Variable | | | Extraction recovery (%) | | |
|-----|----------|---|-----|-------------------------|-----|-----|
| | A | B | C | Ala | Atz | Met |
| 1 | 90 | 5 | 100 | 37 | 30 | 45 |
| 2 | 90 | 5 | 125 | 58 | 54 | 67 |
| 3 | 120 | 5 | 125 | 55 | 52 | 64 |
| 4 | 75 | 6 | 140 | 52 | 52 | 68 |
| 5 | 90 | 7 | 125 | 30 | 22 | 41 |
| 6 | 75 | 4 | 110 | 52 | 48 | 61 |
| 7 | 60 | 5 | 125 | 45 | 43 | 62 |
| 8 | 90 | 3 | 125 | 35 | 31 | 49 |
| 9 | 90 | 5 | 125 | 55 | 53 | 70 |
| 10 | 110 | 4 | 140 | 38 | 33 | 50 |
| 11 | 110 | 4 | 110 | 49 | 44 | 61 |
| 12 | 75 | 6 | 110 | 29 | 16 | 37 |
| 13 | 90 | 5 | 125 | 56 | 55 | 69 |
| 14 | 110 | 6 | 140 | 54 | 54 | 72 |
| 15 | 90 | 5 | 150 | 41 | 38 | 57 |
| 16 | 75 | 4 | 140 | 36 | 31 | 48 |
| 17 | 110 | 6 | 110 | 32 | 25 | 39 |
| 18 | 90 | 5 | 125 | 59 | 57 | 71 |

Table S2 Predicted densities and viscosities of individual components and the related DESs at 25 °C.

| Component | Density (g/mL) | Viscosity (cP) |
|-------------------|----------------|----------------|
| Thym (pure) | 0.956 | 6.13 |
| Hex (pure) | 0.810 | 7.25 |
| Oct (pure) | 0.819 | 12.26 |
| Dec (pure) | 0.826 | 21.45 |
| Dodec (pure) | 0.829 | 37.46 |
| Thym: Hex (2:1) | 0.911 | 4014.86 |
| Thym: Oct (2:1) | 0.907 | 7084.25 |
| Thym: Dec (2:1) | 0.902 | 12986.42 |
| Thym: Dodec (2:1) | 0.899 | 21599.67 |

Table S3 Analysis of variance (ANOVA) for response surface linear and quadratic model for Ala.

| Source | Sum of squares | Degrees of freedom | Mean square | F-value | P-value probe >P |
|----------------|----------------|--------------------|-------------|---------|------------------|
| Model | 1811.55 | 9 | 201.28 | 55.62 | < 0.0001 |
| A | 50.78 | 1 | 50.78 | 14.03 | 0.0057 |
| B | 22.03 | 1 | 22.03 | 6.09 | 0.0389 |
| C | 42.10 | 1 | 42.10 | 11.63 | 0.0092 |
| A ² | 77.53 | 1 | 77.53 | 21.42 | 0.0017 |
| B ² | 845.84 | 1 | 845.84 | 233.73 | < 0.0001 |
| C ² | 486.93 | 1 | 486.93 | 134.55 | < 0.0001 |
| AB | 4.67 | 1 | 4.67 | 1.29 | 0.2889 |
| AC | 2.50 | 1 | 2.50 | 0.69 | 0.4299 |
| BC | 648.00 | 1 | 648.00 | 179.06 | < 0.0001 |
| Residual | 28.95 | 8 | 3.62 | -- | -- |
| Lack of fit | 18.95 | 5 | 3.79 | 1.14 | 0.4889 |
| Pure error | 10.00 | 3 | 3.33 | -- | -- |
| Total | 1840.50 | 17 | -- | -- | -- |

Table S4 Analysis of variance (ANOVA) for response surface linear and quadratic model for Atz.

| Source | Sum of squares | Degrees of freedom | Mean square | F-value | P-value probe >P |
|----------------|----------------|--------------------|-------------|------------|------------------|
| Model | 2822.49 | 9 | 313.61 | 48.70 | < 0.0001 |
| A | 63.73 | 1 | 63.73 | 9.90 | 0.0137 |
| B | 51.78 | 1 | 51.78 | 8.04 | 0.0220 |
| C | 184.64 | 1 | 184.64 | 28.68 | 0.0007 |
| A ² | 86.59 | 1 | 86.59 | 13.45 | 0.0063 |
| B ² | 1141.82 | 1 | 1141.82 | 177.33 | < 0.0001 |
| C ² | 670.59 | 1 | 670.59 | 104.15 | < 0.0001 |
| AB | 23.03 | 1 | 23.03 | 3.58 | 0.0952 |
| AC | 2.203E-004 | 1 | 2.203E-004 | 3.421E-005 | 0.9955 |
| BC | 1081.13 | 1 | 1081.13 | 167.90 | < 0.0001 |
| Residual | 51.51 | 8 | 6.44 | -- | -- |
| Lack of fit | 42.76 | 5 | 8.55 | 2.93 | 0.2025 |
| Pure error | 8.75 | 3 | 2.92 | -- | -- |
| Total | 2874.00 | 17 | -- | -- | -- |

Table S5 Analysis of variance (ANOVA) for response surface linear and quadratic model for Met.

| Source | Sum of squares | Degrees of freedom | Mean square | F-value | P-value probe >P |
|----------------|----------------|--------------------|-------------|---------|------------------|
| Model | 2351.47 | 9 | 261.27 | 79.96 | < 0.0001 |
| A | 18.07 | 1 | 18.07 | 5.53 | 0.0466 |
| B | 26.48 | 1 | 26.48 | 8.10 | 0.0216 |
| C | 256.70 | 1 | 256.70 | 78.56 | < 0.0001 |
| A ² | 57.27 | 1 | 57.27 | 17.53 | 0.0031 |
| B ² | 834.24 | 1 | 834.24 | 255.30 | < 0.0001 |
| C ² | 513.72 | 1 | 513.72 | 157.21 | < 0.0001 |
| AB | 2.92 | 1 | 2.92 | 0.89 | 0.3722 |
| AC | 2.69 | 1 | 2.69 | 0.82 | 0.3910 |
| BC | 968.00 | 1 | 968.00 | 296.24 | < 0.0001 |
| Residual | 26.14 | 8 | 3.27 | -- | -- |
| Lack of fit | 17.39 | 5 | 3.48 | 1.19 | 0.4719 |
| Pure error | 8.75 | 3 | 2.92 | -- | -- |
| Total | 2377.61 | 17 | -- | -- | -- |

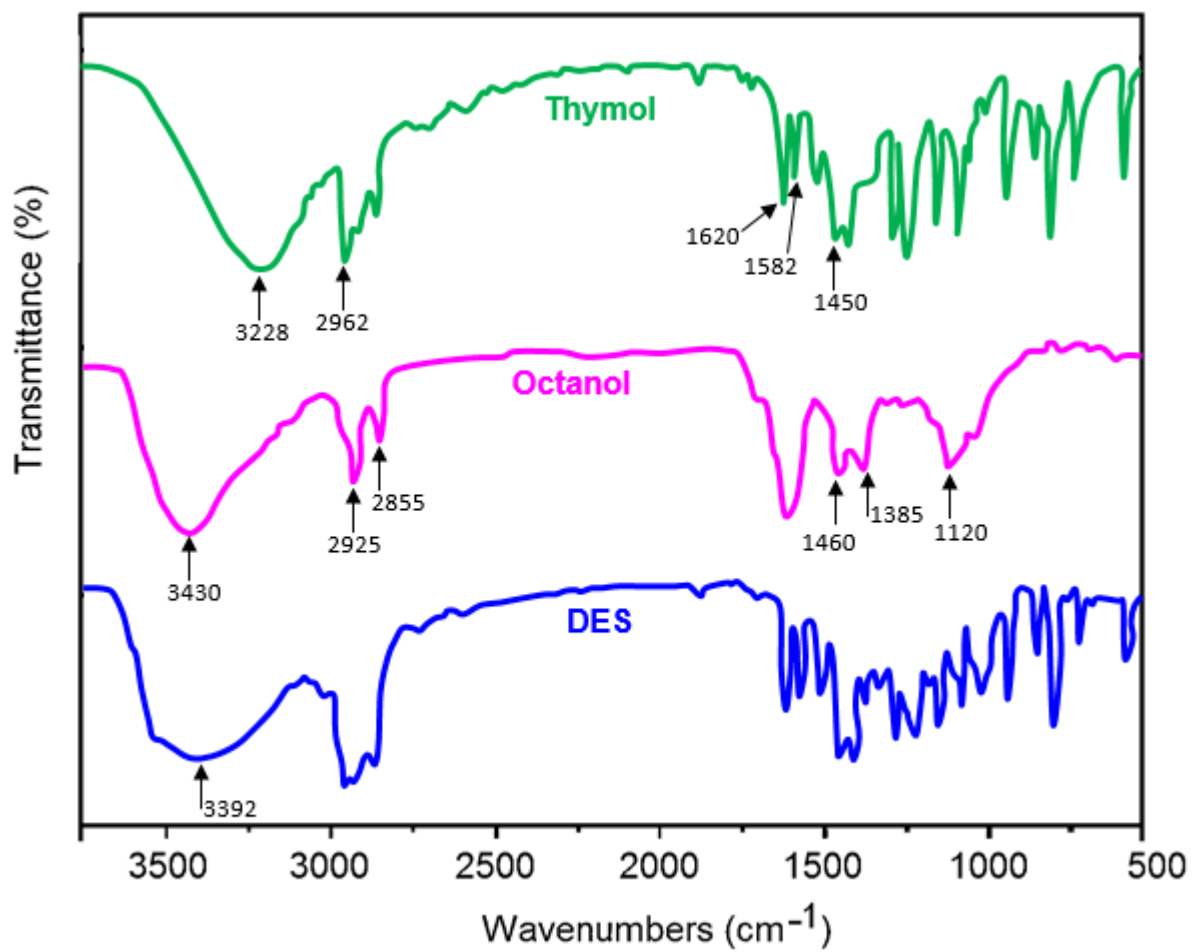


Fig S1: FT-IR spectra of Thym, Oct, and Thym: Oct (2:1).

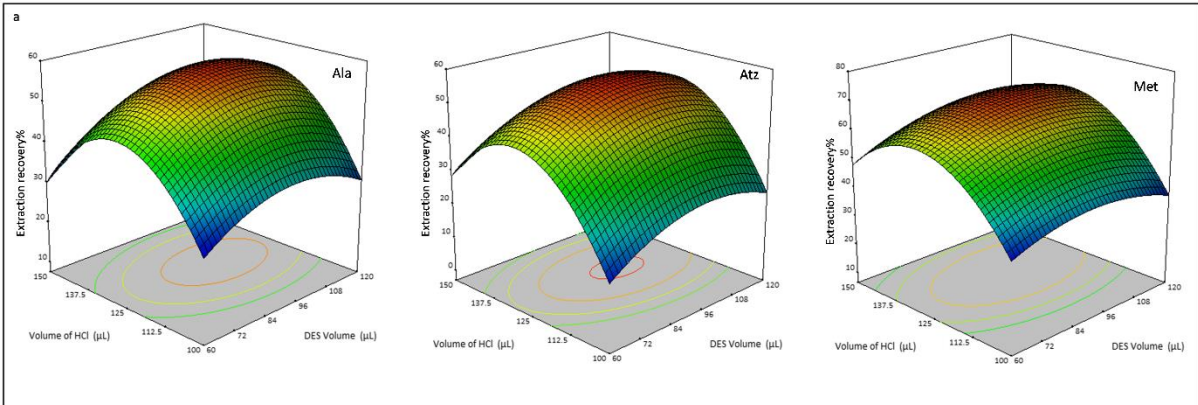
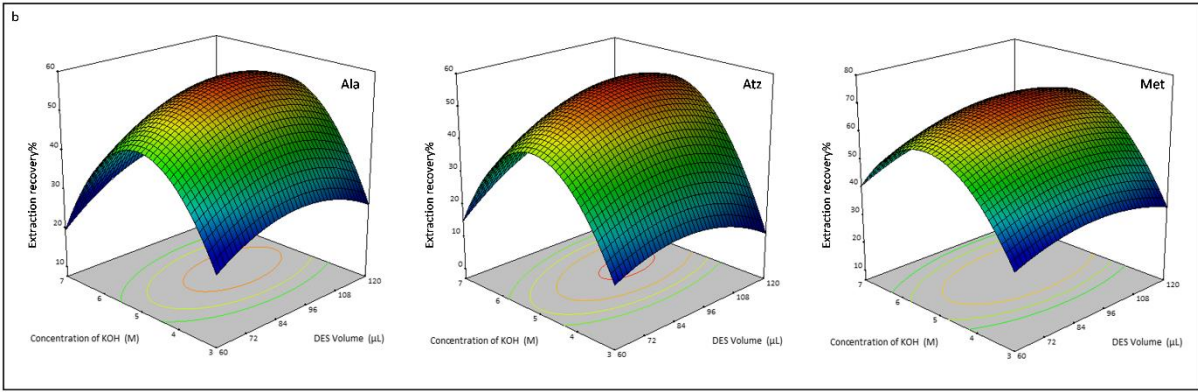
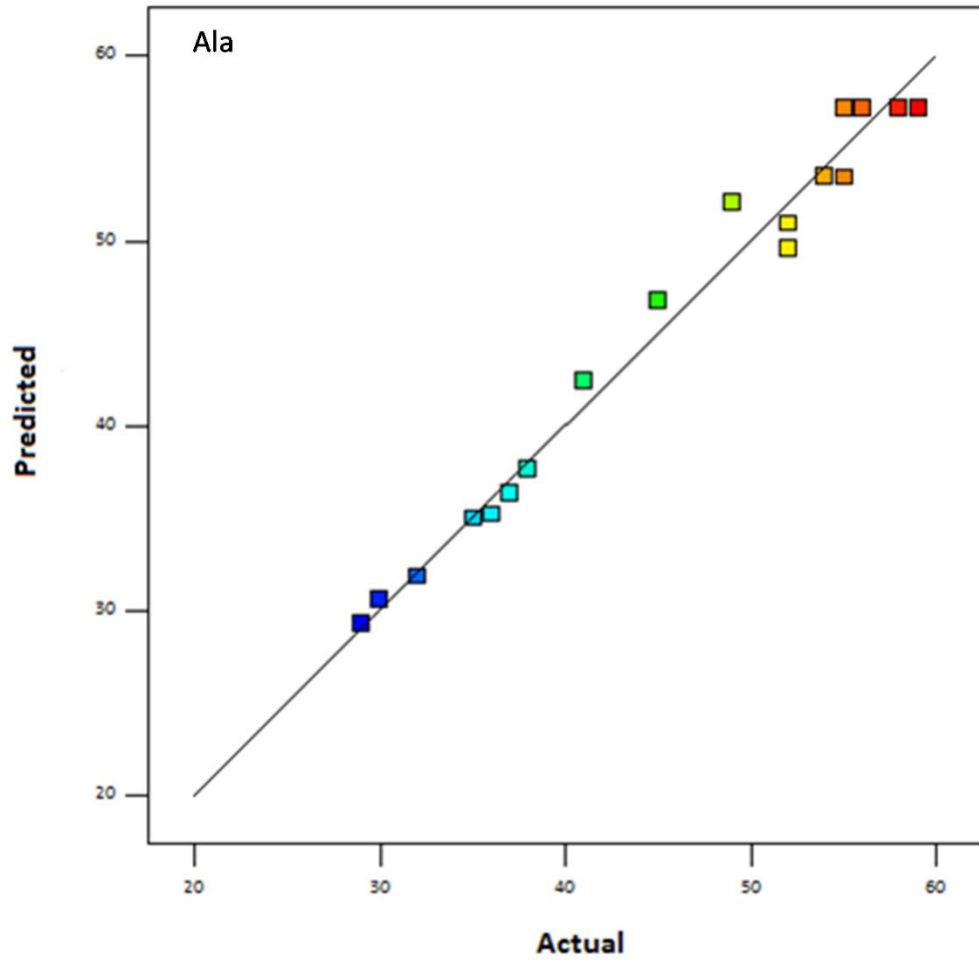
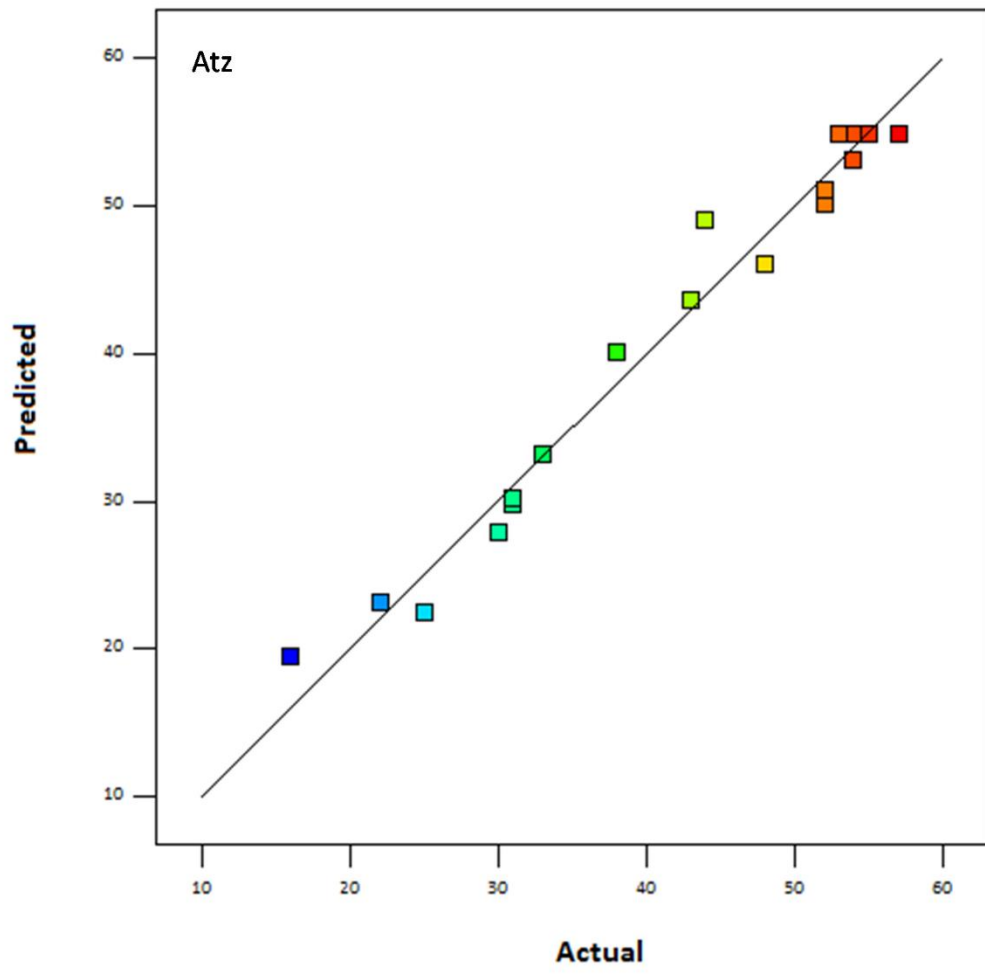


Fig S2: Three-dimensional response surfaces of correlation of (a) concentration of KOH and volume of DES (b) volume of HCl and DES.





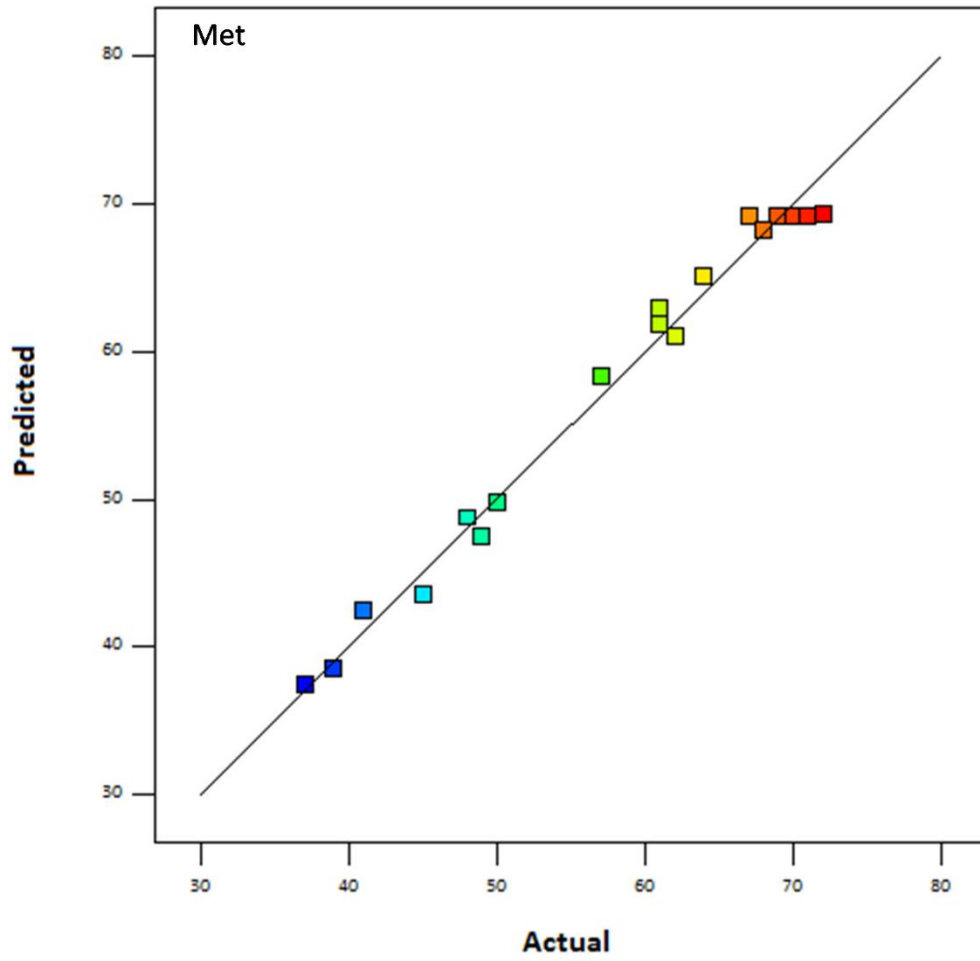


Fig S3: Plot of predicted versus observed values for recovery of herbicides.