# Electronic Supplementary Information

## Magnetic solid-phase extraction of pyrethroid and neonicotinoid insecticides separately in environmental water samples based on alkaline or acidic group-functionalized mesoporous silica

Rui Han, Fei Wang, Chuanfeng Zhao, Meixing Zhang, Shihai Cui*, Jing Yang*

*Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biomedical Materials, College of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Materials Cycling and Pollution Control, Jiangsu Open Laboratory of Major Scientific Instrument and Equipment, Nanjing Normal University, 1 Wenyuan Road, Nanjing, 210023, China.*

*Corresponding author:

Jing Yang Tel.: +86 25 85891705. E-mail address: chemyangjing@njnu.edu.cn.

Shihai Cui Tel.: +86 25 85891705. E-mail address: cuishihai@njnu.edu.cn.

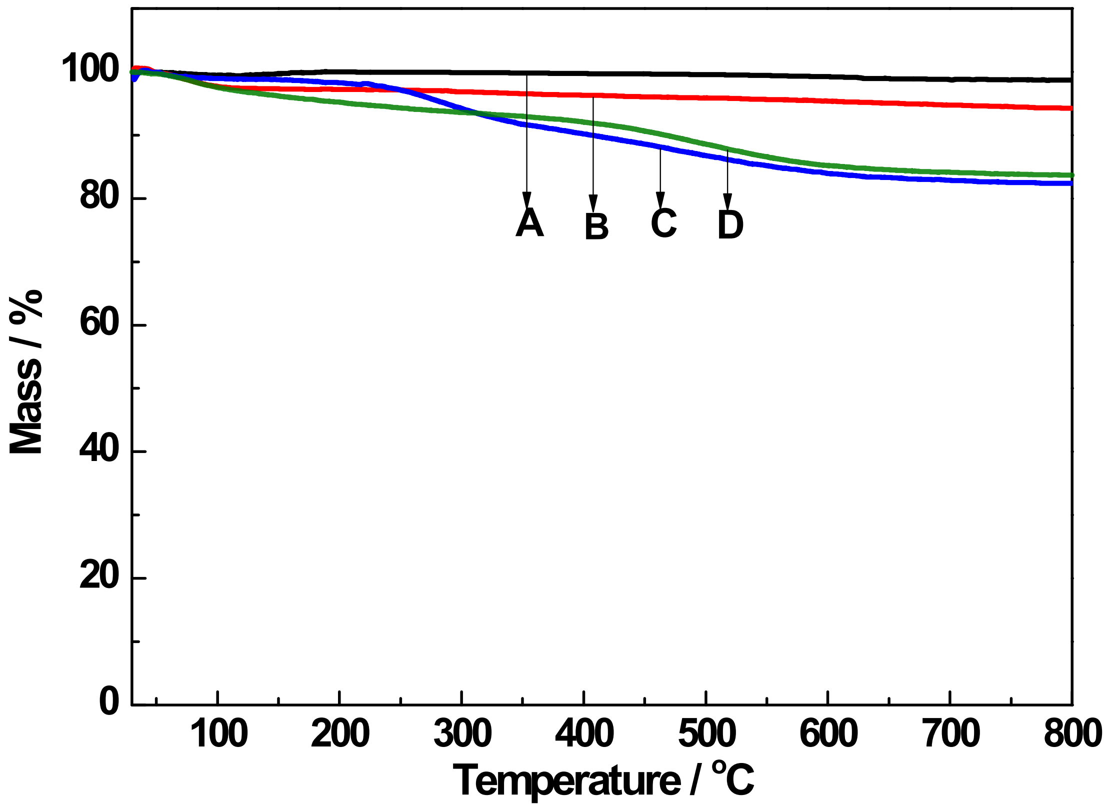



**Fig. S1**. TGA diagrams of $Fe_3O_4$ (A), $Fe_3O_4$@$SiO_2$@KIT-6 (B), FKN (C) and FKC (D).

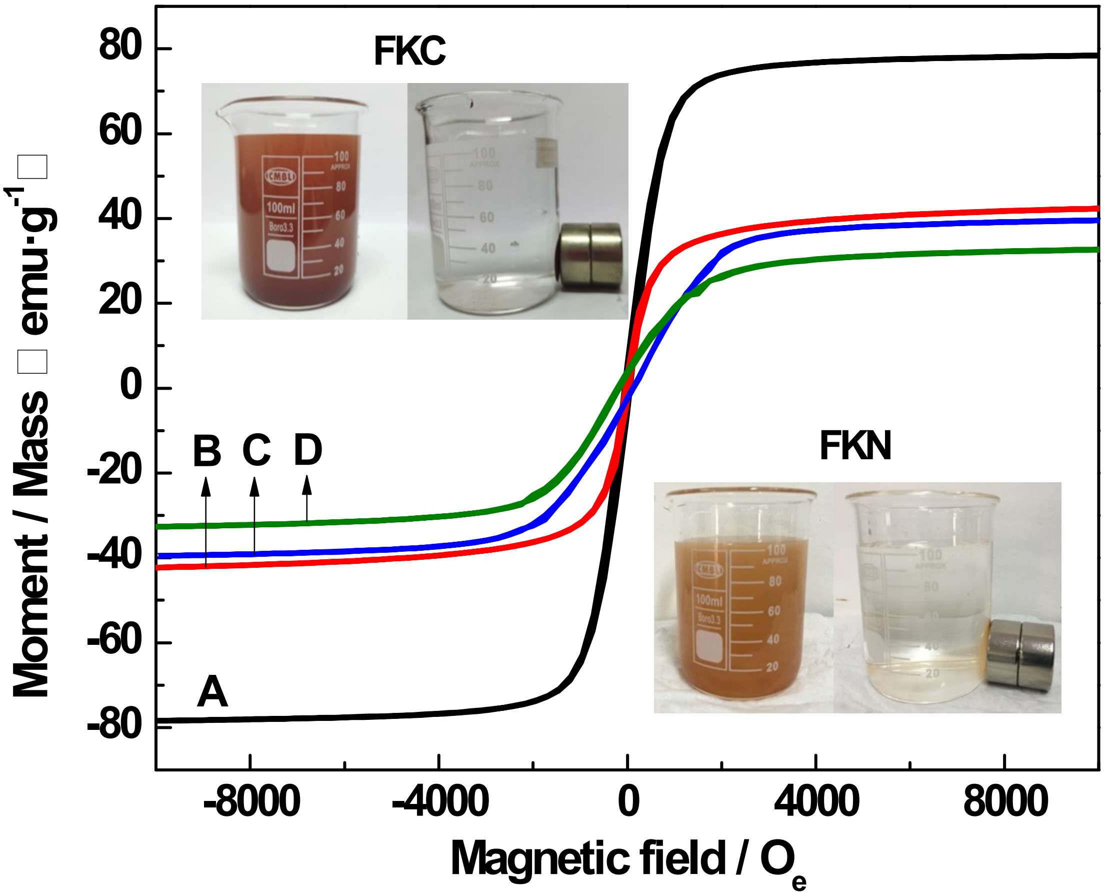



**Fig. S2**. Magnetic property of $Fe_3O_4$ (A), $Fe_3O_4$@$SiO_2$@KIT-6 (B), FKN (C) and FKC (D).

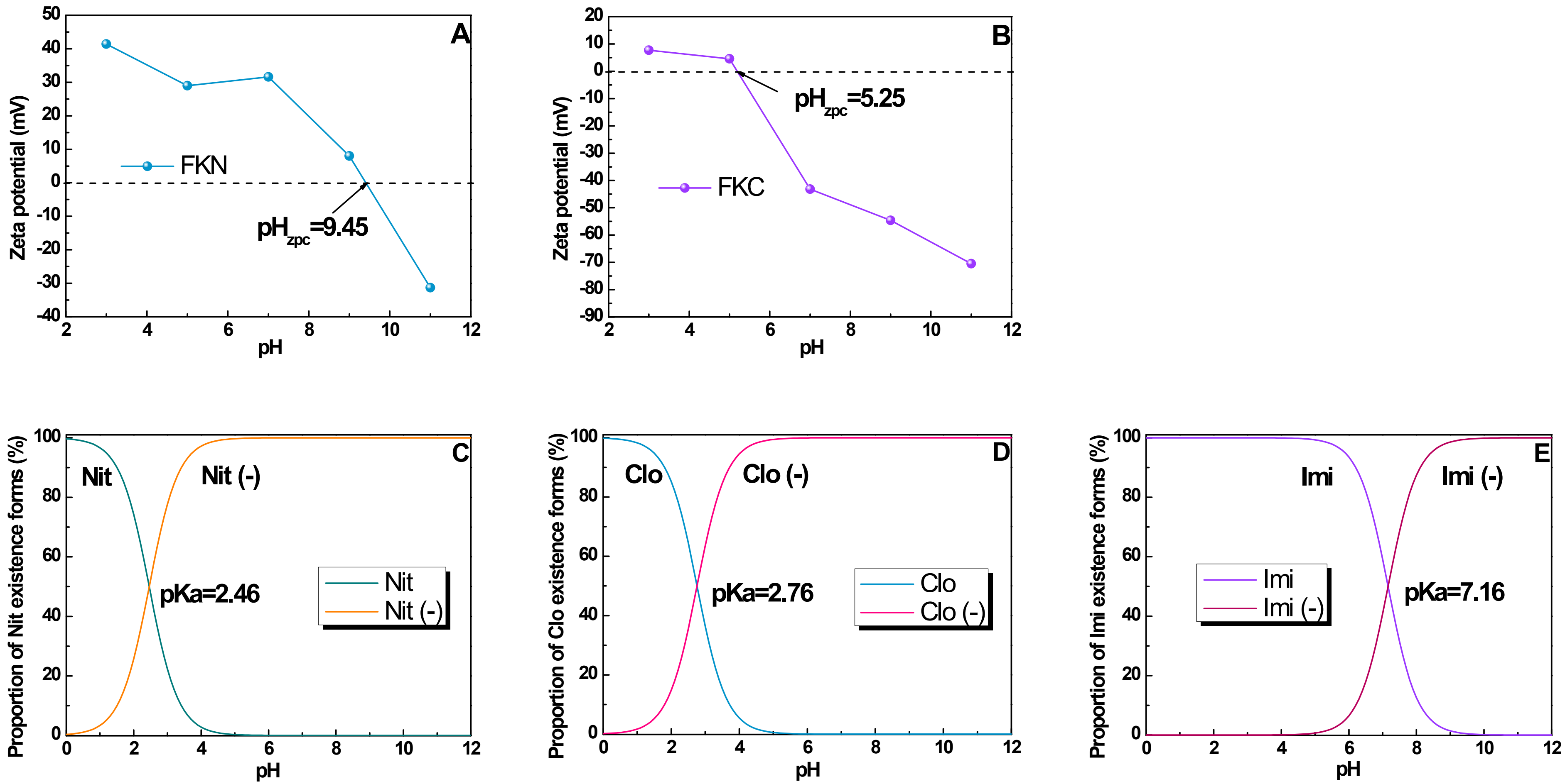



**Fig. S3**. Zeta potential of FKN (A) and FKC (B); The morphological distribution of Nit (C), Clo (D) and Imi (E).

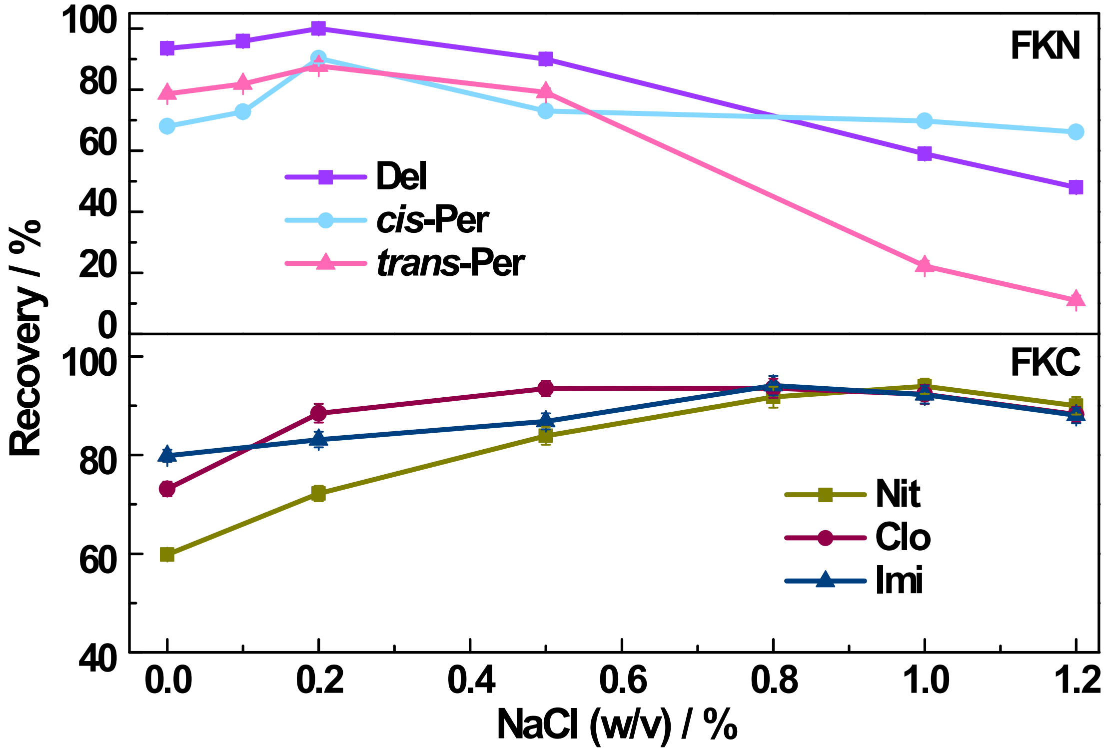
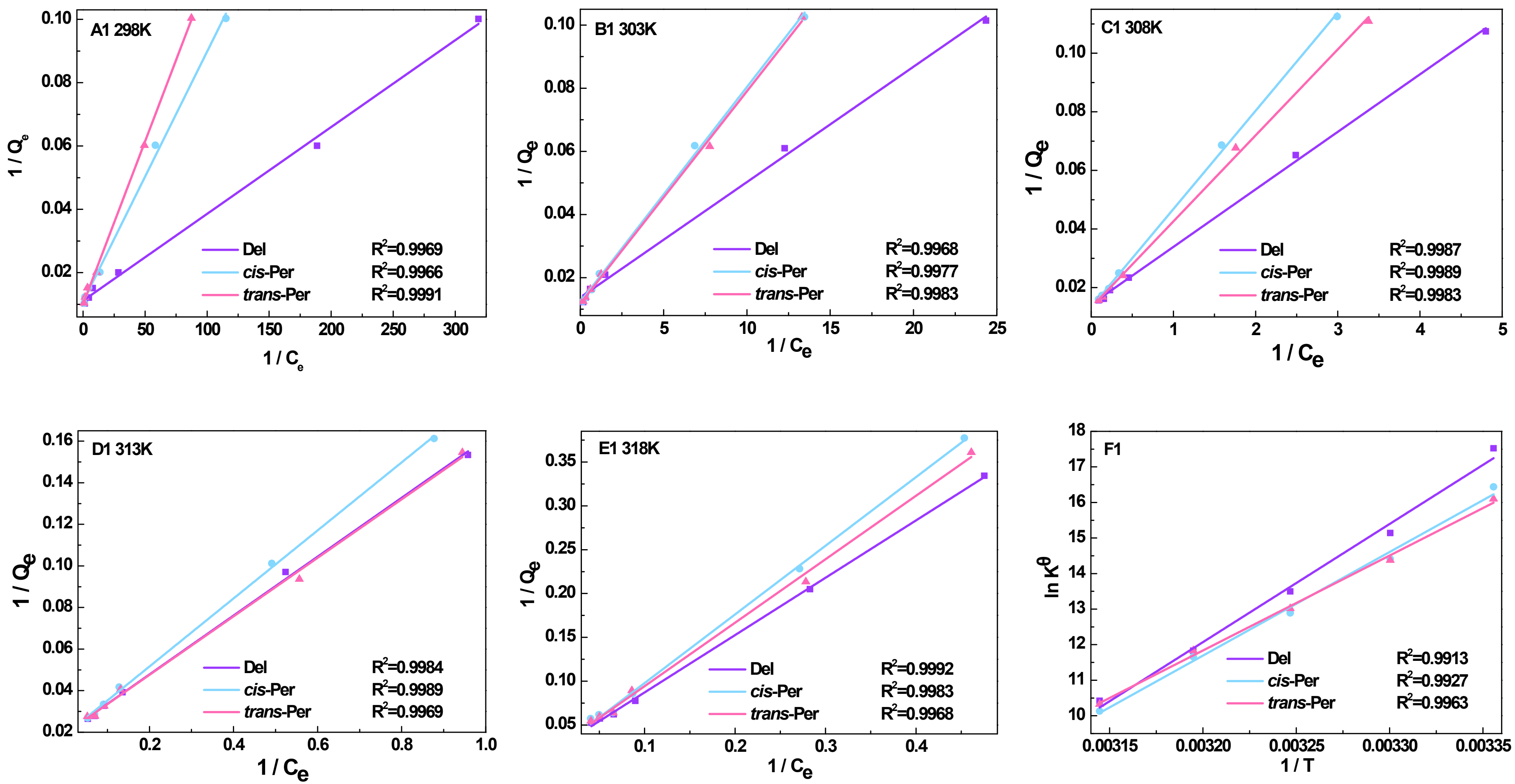



**Fig. S4**. Effect of NaCl concentration for MSPE.



A1 298K
B1 303K
C1 308K
D1 313K
E1 318K
F1
1 / Qe
1 / Ce
ln Kθ
1 / T
Del R2=0.9969
cis-Per R2=0.9966
trans-Per R2=0.9991
Del R2=0.9968
cis-Per R2=0.9977
trans-Per R2=0.9983
Del R2=0.9987
cis-Per R2=0.9989
trans-Per R2=0.9983
Del R2=0.9984
cis-Per R2=0.9989
trans-Per R2=0.9969
Del R2=0.9992
cis-Per R2=0.9983
trans-Per R2=0.9968
Del R2=0.9913
cis-Per R2=0.9927
trans-Per R2=0.9963

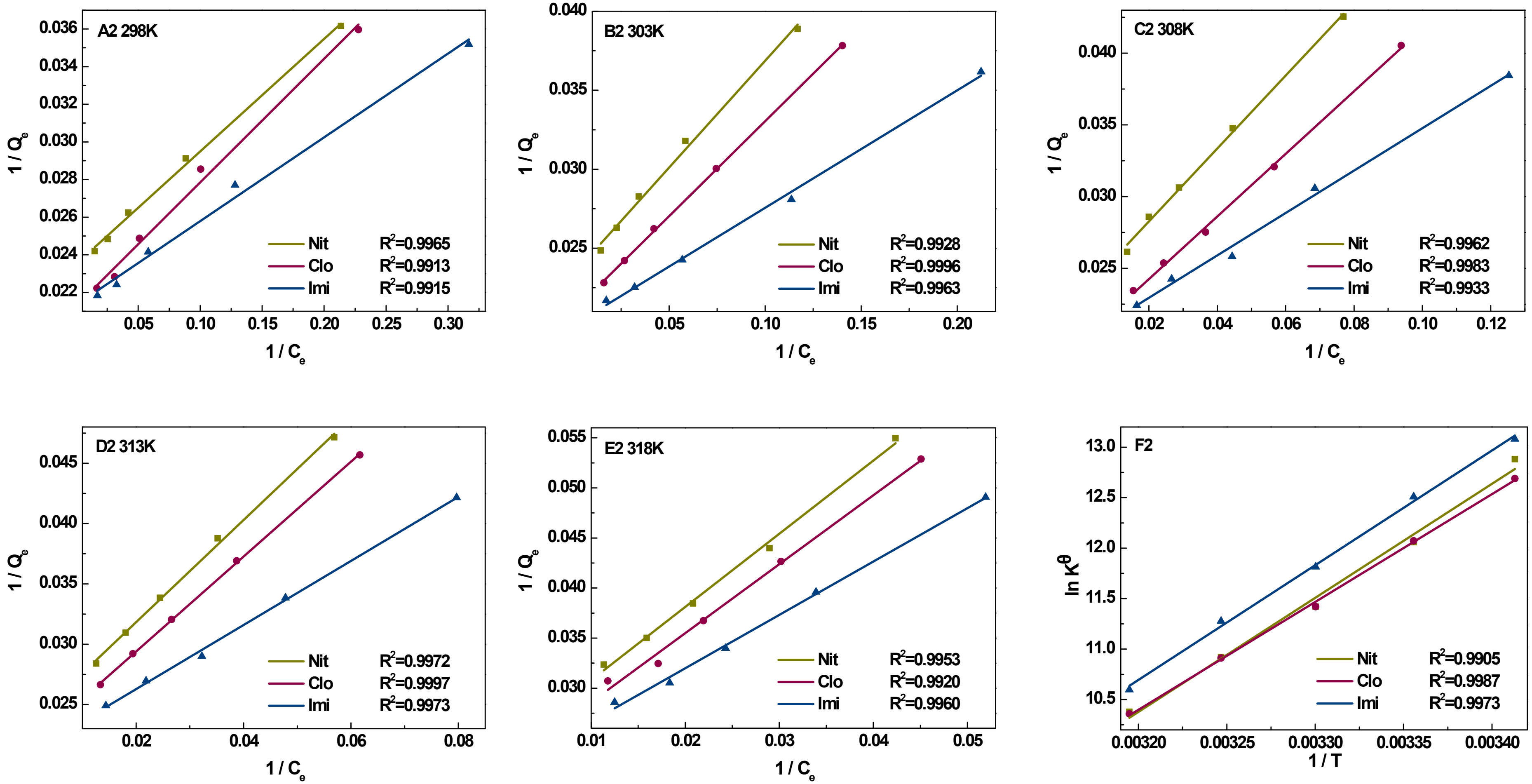



**Fig. S5**. Thermodynamic analysis for the adsorption of insecticides on the FKN (A1-F1) and FKC (A2-F2).

**Table S1**. The chemical structures of the analytes.

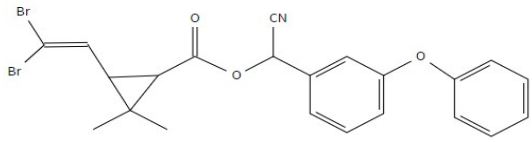
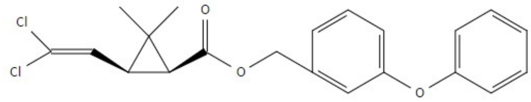
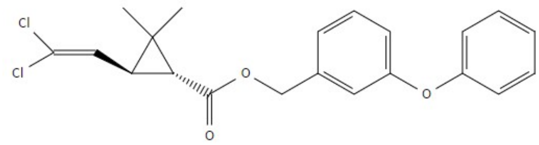
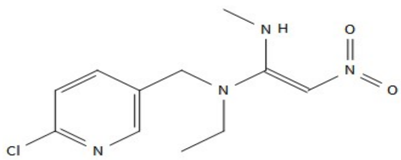
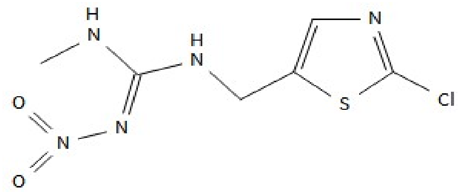
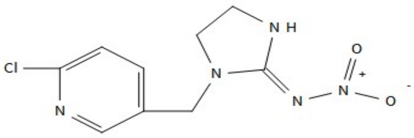
| Analyte | CAS | Structure |
|---|---|---|
| Del | 52918-63-5 |  |
| *cis*-Per | 61949-76-6 |  |
| *trans*-Per | 61949-77-7 |  |
| Nit | 150824-47-8 |  |
| Clo | 210880-92-5 |  |
| Imi | 138261-41-3 |  |

**Table S2**. Formulae of adsorption kinetic and isotherm experiments.

| | | |
|---|---|---|
| $Q_t = \frac{(C_0 - C_t)V}{m}$ | Adsorption capacity | (1) |
| $\ln\left(Q_e - Q_t\right) = lnQ_e - k_1 t$ | Pseudo-first order | (2) |
| $\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$ | Pseudo-second order | (3) |
| $Q_t = k_p t^{\frac{1}{2}} + C$ | Intra-particle model | (4) |
| $\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{K_L Q_{max} C_e}$ | Langmuir equation | (5) |
| $logQ_e = logK_F + \frac{1}{n} logC_e$ | Freundlich equation | (6) |
| $lnK^{\theta} = - \frac{\Delta H^{\theta}}{RT} + \frac{\Delta S^{\theta}}{R}$ | Van't Hoff equation | (7) |
| $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$ | Gibbs function definition | (8) |
| $K^{\theta} = 10^6 K_L$ | | (9) |

$Q_t$: the adsorbed amount in the time t (μg·mg$^{-1}$); $C_0$: the original insecticide concentrations (μg·mL$^{-1}$); $C_t$: the insecticide concentration in time t (μg·mL$^{-1}$); V: the solution volume (mL); m: the mass of the adsorbent (mg); $Q_e$: the amounts of insecticide adsorbed at equilibrium (μg·mg$^{-1}$); $k_1$: the pseudo first-order rate constant (min$^{-1}$); $k_2$: the pseudo-second order adsorption rate constant (mg·μg$^{-1}$·min$^{-1}$); $k_p$: the intra-particle diffusion rate constant (μg·mL$^{-1}$·min$^{-1/2}$); C: the intercept of intra-particle model; $Q_{max}$: the maximum monolayer capacity of the adsorbent (μg·mg$^{-1}$); $K_L$: the Langmuir binding constant (mL·μg$^{-1}$); $C_e$: the equilibrium concentration of analytes in solution (μg·mL$^{-1}$); $K_F$: the Freundlich constant (mL·μg$^{-1}$); n: the heterogeneity factor (dimensionless); $\Delta G^{\theta}$: the Gibbs free energy (kJ·mol$^{-1}$); $\Delta H^{\theta}$: the enthalpy (kJ·mol$^{-1}$); $\Delta S^{\theta}$: the entropy (J·mol$^{-1}$·K$^{-1}$); R: the perfect gas constant (8.314 J·mol$^{-1}$·K$^{-1}$); T: the reaction temperature (K); $K^{\theta}$: the equilibrium constant (dimensionless).

**Table S3**. Physicochemical data of the nanomaterials.

| Materials | $S_{BET}$[a] (m$^2$·g$^{-1}$) | $V_{pore}$[b] (cm$^3$·g$^{-1}$) | $R_{pore}$[c] (nm) |
|---|---|---|---|
| $Fe_3O_4$@$SiO_2$@KIT-6 | 579 | 0.42 | 6.3 |
| FKN | 279 | 0.21 | 8.4 |
| FKC | 549 | 0.86 | 12.4 |

a. Specific surface area; b. Pore volume; c. Pore diameter

**Table S4**. Method evaluation for the MSPE of the pyrethroid and neonicotinoid insecticides.

| Material | Analyte | Linear range / μg·L$^{-1}$ | Calibration curves | Correlation coefficient / r | RSD / % (n=6) | LOD / μg·L$^{-1}$ | LOQ / μg·L$^{-1}$ |
|---|---|---|---|---|---|---|---|
| FKN | Del | 0.12-1200 | y=36.17x-335.08 | 0.9993 | 0.89 | 0.04 | 0.12 |
| | *cis*-Per | 0.06-1200 | y=18.76x+396.65 | 0.9987 | 1.06 | 0.02 | 0.06 |
| | *trans*-Per | 0.30-1200 | y=18.38x-551.22 | 0.9985 | 2.06 | 0.09 | 0.30 |
| FKC | Nit | 1.10-1200 | y=90.054x+767.29 | 0.9996 | 2.12 | 0.33 | 1.11 |
| | Clo | 0.90-1200 | y=65.396x+610.03 | 0.9999 | 1.20 | 0.27 | 0.91 |
| | Imi | 0.75-1200 | y=75.607x+274.51 | 0.9998 | 1.32 | 0.23 | 0.76 |

**Table S5**. The precision of HPLC instrument.

| Material | Analyte | Linear range / μg·L$^{-1}$ | Calibration curves | Correlation coefficient / r | RSD / % (n=3) | LOD / μg·L$^{-1}$ | LOQ / μg·L$^{-1}$ |
|---|---|---|---|---|---|---|---|
| FKN | Del | 6.10-1200 | y=13.71x+938.37 | 0.9998 | 0.092 | 1.84 | 6.10 |
| | *cis*-Per | 3.65-1200 | y=15.66x+423.05 | 0.9989 | 0.102 | 1.10 | 3.65 |
| | *trans*-Per | 14.25-1200 | y=12.19x-653.67 | 0.9957 | 0.141 | 4.32 | 14.26 |
| FKC | Nit | 58.80-1200 | y=26.09x+561.83 | 0.9999 | 0.028 | 17.82 | 58.81 |
| | Clo | 39.20-1200 | y=59.73x-432.75 | 0.9963 | 0.002 | 11.88 | 39.20 |
| | Imi | 39.47-1200 | y=42.97x-185.67 | 0.9980 | 0.002 | 11.96 | 39.47 |

**Table S6**. Kinetic parameters corresponding to different models.

| Material | | Pseudo-first order | | | Pseudo-second order | | | Intra-particle diffusion order | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Q_{e,exp}$ / μg·mg$^{-1}$ | $R^2$ | $K_1$ / min$^{-1}$ | $Q_{e,cal}$ / μg·mg$^{-1}$ | $R^2$ | $K_2$ / mg·μg$^{-1}$·min$^{-1}$ | $Q_{e,cal}$ / μg·mg$^{-1}$ | $R^2$ | $K_p$ / μg·mL$^{-1}$·min$^{-0.5}$ | C |
| FKN | Del | 1.67 | 0.7389 | 0.66 | 2.00 | 0.9986 | 0.60 | 1.81 | 0.9252 | 0.31 | 0.75 |
| | *cis*-Per | 1.47 | 0.8907 | 0.40 | 1.93 | 0.9976 | 0.12 | 2.08 | 0.9891 | 0.49 | -0.04 |
| | *trans*-Per | 1.43 | 0.8794 | 0.52 | 0.95 | 0.9972 | 0.72 | 1.56 | 0.7720 | 0.28 | 0.61 |
| FKC | Nit | 1.18 | 0.8601 | 0.33 | 0.53 | 0.9938 | 0.42 | 1.32 | 0.9744 | 0.32 | 0.21 |
| | Clo | 1.14 | 0.9592 | 0.40 | 0.38 | 0.9951 | 0.77 | 1.10 | 0.9729 | 0.23 | 0.34 |
| | Imi | 1.15 | 0.9626 | 0.57 | 0.72 | 0.9970 | 0.64 | 1.16 | 0.9762 | 0.26 | 0.30 |

**Table S7**. Thermodynamic data based on Van't Hoff equation for the adsorption of insecticides on the FKN and FKC.

| | $K^{\theta}$ ($10^4$) | | | | | $\Delta S^{\theta}$ ($J \cdot mol^{-1} \cdot K^{-1}$) | $\Delta H^{\theta}$ ($kJ \cdot mol^{-1}$) | $\Delta G^{\theta}$ ($kJ \cdot mol^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 293 K | 298 K | 303 K | 308 K | 313 K | | | 293 K | 298 K | 303 K | 308 K | 313 K |
| Del | 4067.04 | 376.16 | 72.69 | 13.76 | 3.35 | -783.93 | -276.34 | -42.73 | -38.81 | -34.89 | -30.97 | -27.05 |
| *cis*-Per | 1376.45 | 180.62 | 39.67 | 11.55 | 2.51 | -678.21 | -242.32 | -40.21 | -36.82 | -33.43 | -30.04 | -26.65 |
| *trans*-Per | 979.61 | 174.89 | 45.13 | 13.81 | 3.04 | -612.21 | -222.07 | -39.63 | -36.57 | -33.51 | -30.44 | -27.38 |
| Nit | 39.31 | 17.27 | 9.12 | 5.52 | 3.21 | -214.22 | -93.91 | -31.14 | -30.07 | -29.00 | -27.93 | -26.86 |
| Clo | 32.40 | 17.48 | 9.11 | 5.48 | 3.15 | -197.70 | -88.80 | -30.87 | -29.88 | -28.90 | -27.91 | -26.92 |
| Imi | 47.92 | 27.06 | 13.51 | 7.90 | 4.00 | -213.37 | -94.46 | -31.95 | -30.88 | -29.81 | -28.75 | -27.68 |