A simple and benign protocol for the synthesis of deep eutectic solvents-based hydrophilic molecularly imprinted resin in water for excellent selective molecular recognition in aqueous phase

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Chemicals and reagents

All chemicals and reagents are commercially available and were used without further pre-treatment. 3-Aminophenol (99%) and forchlorfenuron (98%) were purchased from J&K Scientific Co., Ltd. (Beijing, China). Hexamethylenetetramine (99%) was obtained from Huadong Chemical Co., Ltd. (Tianjin, China). Choline chloride (98%), ethyl glycol (98%), 1,2-propanediol (98%), 1,3-propanediol (98%), and 1,4-butanediol (98%) were purchased from Guangfu Chemical Co., Ltd. (Tianjin, China). Trifluoroacetic acid (TFA) (HPLC grade, 99.5%) were purchased from Kermel Chemical Co., Ltd. (Tianjin, China). 4,4'-Dichlorobenzhydrol (98%) was obtained from Tokyo Chemical Industry Co., Ltd. (Japan). Thidiazuron (analytical standard), 6benzyladenine (99%), ametryn (98.8%), terbutryne (99%), gibberellin (analytical standard), and sulfadimidine sodium (99%) were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Methanol (HPLC grade, 99.9%) was obtained from Xingke Biochem. Co., Ltd. (Shanghai, China). Ultrapure water was filtered using a 0.45 μm membrane before use.

Characterization of DES-HMIR

The morphology of the synthesized DES-HMIR was evaluated by scanning electron microscopy (SEM) using a Phenom Pro SEM system (Phenom, Eindhoven, Netherlands). The GOLD-SIM freeze dryer was obtained from SIM International Group (California, USA). Infrared spectra (IR) were recorded on a Vertex70 Fourier transform infrared spectrometer (Bruker, Karlsruhe, Germany) in the range 400–4000 cm⁻¹ via ATR method. The specific surface area of DES-HMIR was carried out by a

TriStar II 3020 automated pore size and surface area analyzer (Micromeritics, Norcross, USA). Elemental analysis for C, H, O, N was evaluated on an elemental analyzer (Elementar UNICUBE, Germany) and for Cl was performed on energy-dispersive X-ray spectroscopy (Bruker XFlash 6130, ZEISS sigma500, Germany). The chromatographic analysis was performed using UltiMate3000 HPLC (Thermo Fisher Scientific, USA), with a Chromeleon 7.2 workstation as the data acquisition system. The chromatographic column (Accucore XL C₁₈ column, 150 mm × 4.6 mm, 4 μ m) was purchased from Thermo Fisher Scientific (Massachusetts, USA). The mobile phase was water–methanol (47:53, v/v, containing 0.1% TFA in water) at a flow rate of 1.0 mL min⁻¹. The wavelength of the UV was set at 278 nm. The injection volume of the sample was 20 μ L.

Adsorption experiments

DES-HMIR (5.0 mg) was dispersed in 2.0 mL of 20 μ g mL⁻¹ of standard solution (thidiazuron and forchlorfenuron) in a centrifuge tube. After shaking for 12 h at 25 °C, the mixture was then centrifuged at 4500 rpm for 5 min, and the upper layer was collected for HPLC analysis to determine the adsorption amounts of the DES-HMIR. The adsorption capacity (Q_e) of DES-HMIR to thidiazuron and forchlorfenuron was calculated as follows:¹

$$Q_e = \frac{(C_i - C_e) \times V}{W} \tag{1}$$

Where Q_e (µg g⁻¹) is the adsorption amount of the DES-HMIR, C_i (µg mL⁻¹) is the initial concentration of thidiazuron and forchlorfenuron, C_e (µg mL⁻¹) is the concentration of thidiazuron and forchlorfenuron reached the adsorption equilibrium,

V(mL) is the volume of the solution, and W(g) is the amount of the DES-HMIR.

Adsorption kinetics

The adsorption kinetics of the synthesized DES-HMIR #15 were investigated as follows: 2.0 mg of DES-HMIR and DES-HNIR was placed in 10 mL centrifuge tubes respectively, to which was added 2 mL of thidiazuron and forchlorfenuron solution at concentrations of 40 μ g mL⁻¹. The mixture was then shaken for the intervals at 25 °C and then the upper layer was determined by HPLC. The adsorption amounts of the DES-HMIR and DES-HNIR was calculated as Eq. (1).

Moreover, to assess the adsorption mechanism of thidiazuron and forchlorfenuron for DES-HMIR and DES-HNIR, the adsorption kinetic data of both DES-HMIR and DES-HNIR, which described by Eq. (2) and Eq. (3), respectively.²

$$ln(Q_{e} - Q_{t}) = lnQ_{e} - k_{1}$$

$$\frac{t}{Q_{t}} = \frac{t}{Q_{e}} + \frac{1}{k_{2}Q_{e}^{2}}$$
(2)
(3)

 Q_e (mg g⁻¹) and Q_t (mg g⁻¹) are the amounts of thidiazuron and forchlorfenuron adsorbed on the adsorbent at equilibrium and time *t* (min), respectively. k_l (min⁻¹) is the Lagergren pseudo-first-order rate constant of adsorption and k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant of adsorption. The results for the DES-HMIR and DES-HNIR were shown in Fig. S1 and S2, Table S3 and S4.

Adsorption isotherms

The isothermal adsorption was performed as follows: DES-HMIR and DES-HNIR (2 mg) was placed into 10 mL centrifuge tubes respectively, to which was added 2 mL of thidiazuron and forchlorfenuron solution, with the concentration ranging from 2 μ g

mL⁻¹ to 100 µg mL⁻¹. The mixture was shaking 6 h at different temperature (298 K, 308 K, 318 K) and the adsorption capacity of the HMIR and HNIR was calculated as Eq. (1). The Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D-R) models were applied to fit the adsorption data to investigate the adsorption mechanism of thidiazuron and forchlorfenuron of DES-HMIR and DES-HNIR.

The Langmuir isotherm model describes that the surfaces of the DES-HMIR and DES-HNIR comprise homogeneous binding sites with identical sorption energies, and that there is no interaction between thidiazuron and forchlorfenuron. The linear form of the Langmuir adsorption equation is described in Eq. (4):³

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_l Q_m} \tag{4}$$

where Q_e (mg g⁻¹) is the adsorption amount of the DES-HMIR and DES-HNIR at equilibrium, C_e (µg mL⁻¹) is the equilibrium concentration of thidiazuron and forchlorfenuron; Q_m (mg g⁻¹) is the amount of thidiazuron and forchlorfenuron at the maximum monolayer; and K_l (mL µg⁻¹) is the Langmuir adsorption equilibrium constant.

The Freundlich isotherm model is an empirical equation that was applied to the interactions between the adsorption heterogeneous surfaces and thidiazuron and forchlorfenuron. It was assumed that, with increasing thidiazuron and forchlorfenuron concentrations, the amount of thidiazuron and forchlorfenuron on the synthesized resin surface also increased. The linear form of the Freundlich adsorption equation is described as:³

$$lnQ_e = lnK_f + \frac{1}{n}lnC_e \tag{4}$$

where K_f and n are Freundlich constants relating to the adsorption capacity and adsorption intensity, respectively. The value for n indicates the adsorption process of thidiazuron and forchlorfenuron. Thus, for n > 1, the adsorption process is favorable.

The Tempkin isotherm model assumes that the heat of adsorption of thidiazuron and forchlorfenuron in the DES-HMIR layer decreases linearly rather than logarithmically. The linear form of the Tempkin adsorption equation is expressed as:³

$$Q_e = B_T ln A_T + B_T ln C_e \tag{5}$$

where A_T is the Tempkin isotherm constant (mL mg⁻¹) relating to the maximum binding energy expressed as $B_T = RT/b$, where *R* is the gas constant (8.314 J mol⁻¹ K⁻¹); *T* is the absolute temperature (K); and *b* is the Tempkin constant related to heat of sorption (J mol⁻¹). Thus, by linearly fitting Q_e and $\ln C_e$, the constants A_T and B_T could be calculated.

The D-R isotherm model can be applied to study whether the adsorption process mechanism of DES-HMIR is physical or chemical, rather than assuming that the DES-HMIR has uniform surface and constant adsorption energy. The D-R isotherm equations are as follows:³

$$lnQ_e = lnQ_m - \beta \varepsilon^2 \tag{6}$$

$$\varepsilon = RT ln(1 + \frac{1}{C_e}) \tag{7}$$

$$E = (2\beta)^{-0.5}$$
(8)

where β is a constant (mol² J⁻²) relating to the adsorption energy, Q_m (mg g⁻¹) is the

adsorption saturation capacity, and ε is the Polanyi potential. E (kJ mol⁻¹) is the average energy that can be calculated using Eq (8). Thus, an E < 8 kJ mol⁻¹ indicates that the adsorption process is a physical reaction, whereas E > 8 kJ mol⁻¹ indicates that the adsorption process is chemical.

The thermodynamic parameters, including the enthalpy change (ΔH), entropy changes (ΔS), and Gibbs free energy change (ΔG), were calculated from the following equations:³

$$K_c = Q_e / C_e \tag{9}$$

$$lnK_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

$$\Delta G = \Delta H - T \Delta S \tag{11}$$

where Q_e is the amount of thidiazuron and forchlorfenuron adsorbed on the DES-HMIR at equilibrium; C_e is the concentration of thidiazuron and forchlorfenuron solution at equilibrium; K_c is the distribution coefficient; and T and R are the system temperature (K) and universal gas constant (8.314 J mol⁻¹ K⁻¹), respectively.

Adsorption selectivity

The selectivity of DES-HMIR and DES-HNIR was performed by choosing several competitive compounds such as 6-benzyladenine, terbutryne, ametryn, gibberellin, and sulfadimidine sodium. In brief, 2 mg of DES-HMIR and DES-HNIR was placed into 10 mL centrifuge tubes respectively, to which was added 2 mL of the targets and the competitive compounds with the concentration of 100 μ g mL⁻¹. After shaking for 6 h at 25 °C, the mixture was centrifuged at 4500 rpm for 5 min, and the supernatant was collected for HPLC analysis to determine the adsorption capacity. The adsorption

capacity of the DES-HMIR and DES-HNIR was calculated as Eq. (1). The Scatchard analysis and imprinting factor (IF) was calculated as Eq. (12) and Eq. (13), respectively.^{4,5}

$$\frac{Q}{C_e} = \frac{Q_{max} - Q}{K_d}$$
(12)
$$IF = \frac{Q_{MIP}}{K_d}$$

$$Q_{NIP}$$
 (13)

Where $Q_{\text{max}} (\text{mg g}^{-1})$ is the maximum binding quantity of DES-HMIR, $K_d (\text{g L}^{-1})$ is dissociation constant, $C_e (\mu \text{g mL}^{-1})$ is the equilibrium concentration of thidiazuron and forchlorfenuron. Q_{MIP} and $Q_{\text{NIP}} (\text{mg g}^{-1})$ are the adsorption capacities of the analytes on DES-HMIR and DES-HNIR, respectively.

Tomato sample pretreatment procedure

The tomato sample purchased from local supermarkets in Baoding city were first homogenized and then 10 g homogenized tomato sample was centrifuged at 15000 rpm for 10 min. The supernatants were transferred into volumetric flasks (10 mL). The residues on the bottom were extracted with 6 mL acetonitrile, and then centrifuged at 15000 rpm for 10 min. After repeated this extraction process at once, the acetonitrile were combined, evaporated until dry, and then redissolved in 1 mL of water, repeated at twice. The reconstituted samples were transferred into the same 10 mL flasks as their supernatants and diluted to the mark with ultrapure water.

5.0 mg of the synthesized DES-HMIR as SPE adsorbent was packed into a pipette tip (200 μ L) with comprising degreased cotton at both ends of the pipette tip. Then a 1.0 mL blue pipette tip was assembled with the pipette tip. The assembled pipette tip

SPE cartridge was preconditioned with 1.0 mL of methanol and water, respectively. Subsequently, the cartridge was loaded with 1.0 mL sample solution and then washed with 1.0 mL water to remove the interferences. Precisely 0.2 mL of acetonitrile–water (1:1, v/v) was used to elute the thidiazuron and forchlorfenuron on the DES-HMIR, then the eluate was injected to HPLC for analysis.

Performance and reusability of DES-HMIR at different pH value

To evaluate the performance of the DES-HMIR under different pH conditions, 5.0 mg of DES-HMIR were loaded in a pipette tip, which sealed with two pieces of cotton at both ends. After preconditioning with 1.0 mL methanol and water respectively, 1.0 mL of sample solution (5.0 μ g mL⁻¹) under different pH conditions (pH 3.0–9.0) was loaded on the pipette tip cartridge, then the adsorbed analytes (thidiazuron and forchlorfenuron) were eluted via 0.2 mL of acetonitrile–water (1:1, v/v). The loading effluent and eluate were for HPLC analysis directly.

To evaluate the reusability of the DES-HMIR under different pH conditions, 5.0 mg of DES-HMIR were loaded in a pipette tip, which sealed with two pieces of cotton at both ends. After preconditioning with 1.0 mL methanol and water respectively, 1.0 mL of sample solution (5.0 μ g mL⁻¹) at pH 3 and pH 9 was loaded on the pipette tip cartridge, then the adsorbed analytes (thidiazuron and forchlorfenuron) were eluted via 0.2 mL of acetonitrile–water (1:1, v/v). At last, the DES-HMIR was eluted with another 0.1 mL of acetonitrile–water (1:1, v/v) to ensure complete removal of the residual analytes adsorbed on DES-HMIR and then reused in the next adsorption-desorption cycle.

Figures and Tables



Fig. S1 Adsorption amount of DES-HMIR synthesized with various types of DES.



Fig. S2 Lagergren pseudo-first-order (a) and pseudo-second-order (b) kinetics models of DES-

HMIR for adsorption of thidiazuron and forchlorfenuron.



Fig. S3 Lagergren pseudo-first-order (a) and pseudo-second-order (b) kinetics models of DES-

HNIR for adsorption of thidiazuron and forchlorfenuron.



Fig. S4 Adsorption isotherm models of DES-HMIR for adsorption of thidiazuron and forchlorfenuron at different temperatures. (a: Langmuir linear fits for thidiazuron; b: Langmuir linear fits for forchlorfenuron; c: Freundlich linear fits for thidiazuron; d: Freundlich linear fits for

forchlorfenuron; e: Tempkin linear fits for thidiazuron; f: Tempkin linear fits for forchlorfenuron;

g: D-R linear fits for thidiazuron; h: D-R linear fits for forchlorfenuron).



Fig. S5 Adsorption isotherm models of DES-HNIR for adsorption of thidiazuron and forchlorfenuron at different temperatures. (a: Langmuir linear fits for thidiazuron; b: Langmuir linear fits for forchlorfenuron; c: Freundlich linear fits for thidiazuron; d: Freundlich linear fits for

forchlorfenuron; e: Tempkin linear fits for thidiazuron; f: Tempkin linear fits for forchlorfenuron;

g: D-R linear fits for thidiazuron; h: D-R linear fits for forchlorfenuron).



Fig. S6 The plots of $\ln K_1$ versus 1/T for thidiazuron and forchlorfenuron of DES-HMIR (a) and

DES-HNIR (b).



Fig. S7 Scatchard plot analysis of DES-HMIR and DES-HNIR for thidiazuron at different temperatures (a: DES-HMIR at 298 K; b: DES-HNIR at 298 K; c: DES-HMIR at 308 K; d: DES-HNIR at 308 K; e: DES-HMIR at 318 K; f: DES-HNIR at 318 K).



Fig. S8 Scatchard plot analysis of DES-HMIR and DES-HNIR for forchlorfenuron at different temperatures (a: DES-HMIR at 298 K; b: DES-HNIR at 298 K; c: DES-HMIR at 308 K; d: DES-

HNIR at 308 K; e: DES-HMIR at 318 K; f: DES-HNIR at 318 K).



Fig. S9 SEM of DES-HMIR before used (a) and after 26 cycles (c).



Fig. S10 Extraction efficiency for the analytes under different pH conditions.



Fig. S11 Reusability of DES-HMIR at different pH conditions (a: adsorption ratio at pH 3; b:

extraction recovery at pH 3; c: adsorption ratio at pH 9; d: extraction recovery at pH 9).

DES-	DES	Hydrogen bond	Hydrogen bond	Molar Ratios
HMIR		acceptor	donor	
MIP-1	DES-1		ethyl glycol	1:2
MIP-2	DES-2		ethyl glycol	1:3
MIP-3	DES-3		ethyl glycol	1:4
MIP-4	DES-4		1,4-butanediol	1:2
MIP-5	DES-5		1,4-butanediol	1:3
MIP-6	DES-6		1,4-butanediol	1:4
MIP-7	DES-7	choline chloride	1,2-propanediol	1:2
MIP-8	DES-8		1,2-propanediol	1:3
MIP-9	DES-9		1,2-propanediol	1:4
MIP-10	DES-10		1,3-propanediol	1:2
MIP-11	DES-11		1,3-propanediol	1:3
MIP-12	DES-12		1,3-propanediol	1:4

Table S1. Synthesis of DES

DES-HMIR	А	В	С	D	Е	F
number	(mmol)	(mmol)	(mL)		(mL)	(mmol)
1	12	6	60	DES-1	1.0	0.24
2	12	6	60	DES-2	1.0	0.24
3	12	6	60	DES-3	1.0	0.24
4	12	6	60	DES-4	1.0	0.24
5	12	6	60	DES-5	1.0	0.24
6	12	6	60	DES-6	1.0	0.24
7	12	6	60	DES-7	1.0	0.24
8	12	6	60	DES-8	1.0	0.24
9	12	6	60	DES-9	1.0	0.24
10	12	6	60	DES-10	1.0	0.24
11	12	6	60	DES-11	1.0	0.24
12	12	6	60	DES-12	1.0	0.24
13	12	6	20	DES-4	1.0	0.24
14	12	6	40	DES-4	1.0	0.24
15	12	6	80	DES-4	1.0	0.24
16	12	6	100	DES-4	1.0	0.24
17	12	6	150	DES-4	1.0	0.24
18	12	6	80	DES-4	1.0	0
19	12	6	80	DES-4	1.0	0.06
20	12	6	80	DES-4	1.0	0.12
21	12	6	80	DES-4	1.0	0.36
22	12	6	80	DES-4	1.0	0.48
23	12	6	80	DES-4	1.0	1.5
24	12	6	80	DES-4	0.5	0.24
25	12	6	80	DES-4	2.0	0.24
26	12	6	80	DES-4	3.0	0.24

Table S2. Synthesis scheme of DES-HMIR

27	12	6	80	DES-4	4.0	0.24
28	12	6	80	DES-4	5.0	0.24

A: 3-Aminophenol; B: Hexamethylenetetramine; C: Volume of water; D: Type of DES; E:

Volume of DES; F: Amount of 4,4'-dichlorobenzhydrol.

DES-HMIR	DES	Types of DES	Composition of DES
MIP-a	DES-a	omine/omide head DES	choline chloride/urea (molar ratio 1:2)
MIP-b	DES-b	amine/amide-based DES	choline chloride/thiourea (molar ratio 1:2)
MIP-c	DES-c		choline chloride/oxalic acid (molar ratio 1:2)
MIP-d	DES-d	carboxync-based DES	choline chloride/propanedioic acid (molar ratio 1:2)
MIP-e	DES-e	alcohol-based DES	choline chloride/1,4-butanediol (molar ratio 1:2)

Table S3. DES for the synthesis of DES-HMIR

Analyte	Pseudo-first-order			Pseudo-second-order		
	$k_l (\mathrm{min}^{-1})$	$Q_e (\mathrm{mg \ g^{-1}})$	R ²	$k_2 ({ m gmin^{-1}mg^{-1}})$	$Q_e (\mathrm{mg \ g^{-1}})$	R ²
thidiazuron	0.0061	4.4552	0.9432	0.0066	16.5262	0.9990
forchlorfenuron	0.0061	6.3737	0.9687	0.0045	21.8818	0.9989

Table S4. Lagergren pseudo-first-order and pseudo-second-order kinetics parameters of DES-

HMIR for the adsorption of thidiazuron and forchlorfenuro	on
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	Ps	eudo-first-order		Pseudo-second-order			
Analyte	k_{l} (min ⁻¹)	$Q_e (\mathrm{mg}\;\mathrm{g}^{-1})$	R ²	$k_2 ({ m gmin^{-1}mg^{-1}})$	$Q_e (\mathrm{mg \ g^{-1}})$	R ²	
thidiazuron	0.0048	1.8116	0.9710	0.0058	2.2249	0.9789	
forchlorfenuron	0.0031	1.1824	0.8531	0.0220	2.3066	0.9972	

Table S5. Lagergren pseudo-first-order and pseudo-second-order kinetics parameters of DES-

HNIR for the adsorption of thidiazuron and forchlorfenur	on
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		Langmuir constants			
I (K)	Analyte —	K_l (mL µg ⁻¹)	$Q_e (\mathrm{mg \ g^{-1}})$	R ²	
202	thidiazuron	0.0218	36.55	0.9879	
298	forchlorfenuron	0.0156	62.34	0.9922	
200	thidiazuron	0.0235	32.56	0.9902	
308	forchlorfenuron	0.0191	50.10	0.9875	
210	thidiazuron	0.0239	29.50	0.9925	
518	forchlorfenuron	0.0221	42.46	0.9869	

Table S6. Langmuir isotherm for the adsorption of analytes on DES-HMIR

		Langmuir constants			
I (K)	Analyte —	K_l (mL µg ⁻¹)	$Q_e (\mathrm{mg \ g}^{-1})$	R ²	
200	thidiazuron	0.0255	3.999	0.9749	
298	forchlorfenuron	0.0068	21.66	0.9957	
200	thidiazuron	0.0259	3.164	0.9464	
308	forchlorfenuron	0.0094	14.02	0.9968	
210	thidiazuron	0.0227	2.816	0.9591	
318	forchlorfenuron	0.0114	9.929	0.9943	

Table S7. Langmuir isotherm for the adsorption of analytes on DES-HNIR

T (K)		Freundlich constants				
	Analyte —	$K_f(\mathrm{mg}~\mathrm{g}^{-1})$	п	R ²		
208	thidiazuron	1.159	1.422	0.9793		
298	forchlorfenuron	1.245	1.280	0.9791		
308	thidiazuron	1.124	1.448	0.9782		
	forchlorfenuron	1.235	1.321	0.9681		
318	thidiazuron	0.992	1.423	0.9680		
	forchlorfenuron	1.226	1.359	0.9637		

Table S8. Freundlich isotherm for the adsorption of analytes on DES-HMIR

T (K)	A	Freundlich constants			
	Analyte —	$K_f(\text{mg g}^{-1})$	п	R ²	
202	thidiazuron	0.1327	1.391	0.9546	
298	forchlorfenuron	0.1742	1.143	0.9947	
308	thidiazuron	0.1028	1.368	0.9222	
	forchlorfenuron	0.1636	1.198	0.9935	
318	thidiazuron	0.0798	1.336	0.9419	
	forchlorfenuron	0.1453	1.234	0.9916	

Table S9. Freundlich isotherm for the adsorption of analytes on DES-HNIR

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T (K)	Analyte	Temp	Tempkin constants			
		A_T	B_T	R ²		
208	thidiazuron	0.3974	6.308	0.9362		
298	forchlorfenuron	0.3549	9.620	0.9328		
308	thidiazuron	0.4093	5.751	0.9424		
	forchlorfenuron	0.3834	8.334	0.9520		
318	thidiazuron	0.4159	5.247	0.9538		
	forchlorfenuron	0.4029	7.460	0.9591		

Table S10. Tempkin isotherm for the adsorption of analytes on DES-HMIR

T (K)	Analyte ——	Temp	bkin constants	
		A_T	B_T	R ²
298	thidiazuron	0.4260	0.7379	0.9622
	forchlorfenuron	0.2907	2.1858	0.8632
308	thidiazuron	0.4559	0.5772	0.9707
	forchlorfenuron	0.3074	1.6997	0.8823
318	thidiazuron	0.4207	0.4966	0.9720
	forchlorfenuron	0.3211	1.3369	0.8966

Table S11. Tempkin isotherm for the adsorption of analytes on DES-HNIR

T (V)	Analyte ——	D-R constants				
I (K)		$Q_e (\mathrm{mg \ g^{-1}})$	E (kJ mol ⁻¹)	R ²		
208	thidiazuron	13.90	0.4597	0.6714		
298	forchlorfenuron	19.58	0.4379	0.6585		
200	thidiazuron	12.89	0.4795	0.6697		
308	forchlorfenuron	18.00	0.4548	0.6868		
210	thidiazuron	11.97	0.4851	0.7025		
318	forchlorfenuron	16.62	0.4754	0.6889		

Table S12. D-R isotherm for the adsorption of analytes on DES-HMIR

Analyte —	D-R constants			
	$Q_e (\mathrm{mg \ g}^{-1})$	E (kJ mol ⁻¹)	R ²	
thidiazuron	1.688	0.4522	0.6715	
orchlorfenuron	3.745	0.4222	0.6046	
thidiazuron	1.388	0.4540	0.7180	
orchlorfenuron	3.058	0.4465	0.6047	
thidiazuron	1.142	0.4656	0.7153	
orchlorfenuron	2.498	0.4664	0.6142	
	Analyte — thidiazuron orchlorfenuron thidiazuron orchlorfenuron thidiazuron	AnalyteD- $Q_e (mg g^{-1})$ $Q_e (mg g^{-1})$ thidiazuron1.688orchlorfenuron3.745thidiazuron1.388orchlorfenuron3.058thidiazuron1.142orchlorfenuron2.498	Analyte D-R constants $Q_e (mg g^{-1})$ $E (kJ mol^{-1})$ thidiazuron 1.688 0.4522 orchlorfenuron 3.745 0.4222 thidiazuron 1.388 0.4540 orchlorfenuron 3.058 0.4465 thidiazuron 1.142 0.4656 orchlorfenuron 2.498 0.4664	

Table S13. D-R isotherm for the adsorption of analytes on DES-HNIR

Analyta	ΔH (kJ mol ⁻¹)	$\Delta S (\mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1})$	$\Delta G (\mathrm{kJ} \mathrm{mol}^{-1})$			R ²
Analyte			298 K	308 K	318 K	
thidiazuron	-7.30	0.07	-27.54	-28.22	-28.90	0.9945
forchlorfenuron	-9.47	0.06	-28.69	-29.33	-29.97	0.9642

Table S14. Thermodynamics parameters for the adsorption of analytes on DES-HMIR

Analyta	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta S (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta G (\mathrm{kJ}\mathrm{mol}^{-1})$			D ²
Analyte			298 K	308 K	318 K	K-
thidiazuron	-15.67	0.02	-22.06	-22.27	-22.49	0.9532
forchlorfenuron	-18.01	0.02	-24.95	-25.18	-25.41	0.9989

Table S15. Thermodynamics parameters for the adsorption of analytes on DES-HNIR

Analytes	temperature	$K_{d, l}$	Q _{max, 1} /	P ²	$K_{d, 2}$	Q _{max, 1} /	P ²
		(g L ⁻¹)	(mg g ⁻¹)	R	(g L ⁻¹)	(mg g ⁻¹)	R
thidiazuron	298 K	2.88	12.08	0.9812	17.22	30.42	0.9023
	308 K	3.08	10.98	0.9946	17.57	27.76	0.9203
	318 K	9.54	19.14	0.9184	30.95	29.48	0.8496
forchlorfenuron	298 K	3.22	26.87	0.9428	16.98	47.68	0.9955
	308 K	5.20	29.55	0.9286	15.91	39.89	0.9648
	318 K	5.74	26.65	0.9902	11.77	33.28	0.9858

Table S16. Scatchard parameters of DES-HMIR at different temperatures

Apolytos	tomporatura	K_{d}	Q _{max} /	D ²
Analytes	temperature	(g L ⁻¹)	(mg g ⁻¹)	K²
	298 K	42.32	4.38	0.8982
thidiazuron	308 K	46.75	3.75	0.6326
	318 K	49.58	3.15	0.7651
	298 K	114.55	19.78	0.9913
forchlorfenuron	308 K	85.84	12.92	0.9900
	318 K	73.86	9.39	0.9878

Table S17. Scatchard parameters of DES-HNIR at different temperatures

Analytas	$Q_{\it DES-HMIR,\ max}$	$Q_{\it DES-HNIR,\ max}$	IE
Analytes	(mg g ⁻¹)	(mg g ⁻¹)	11'
thidiazuron	24.91	2.75	9.06
forchlorfenuron	37.29	8.78	4.25
6-benzyladenine	16.22	4.44	3.65
terbutryne	9.71	7.75	1.25
ametryn	3.82	2.58	1.48
gibberellin	1.09	0.89	1.22
sulfadimidine sodium	0.22	0.68	0.32

Table S18. Selectivity adsorption parameters of DES-HMIR and DES-HNIR

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