Supplementary material

A Carboxyl Group-functionalized Ionic Liquid Hybrid Adsorbent for Solid-phase Extraction and Determination of Trace Diclofenac Sodium in Milk Samples

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Table of contents:

Table S1. The isotherm model and its equations.

Isotherm model	Equation	
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$	(1)
Freundlich	$Inq_e = InK_F + \frac{1}{n} InC_e$	(2)
Tempkin	$q_e = K_T InC_e + K_T Inf$	(3)

where q_e (mg/g) and q_m (mg/g) are, respectively, the equilibrium adsorption capacity and the maximum adsorption capacity. C_e (mg/L) stands for the equilibrium concentration of DS, K_L, K_F and K_T are the constant of Langmuir, Freundlich and Tempkin, respectively, and f is the maximum binding energy.

Table S2. The related parameters of various adsorption isotherm models.

Langmuir model			Freundlich model			Tempkin model		
K_L(L/mg)	q_m(mg/g)	R^2	K_F	n	R^2	K_T(L/mg)	f	R^2
5.15×10^{-4}	965.3	0.9509	0.148	1.71	0.8791	139.4	11.3	0.9264

Table S3. The recovery and enrichment factor of PS-IL-COOH at different concentrations of DS.

V_{DS} (mL)	C_i (μg/mL)	R%	C_f (μg/mL)	EF	RSD (%)
50.0	0.1	99.6	1.66	16.6	0.7
100.0	0.05	99.0	1.65	33.0	1.6
250.0	0.02	99.0	1.65	82.5	0.9
500.0	0.01	96.2	1.60	160.0	1.3
1000.0	0.005	94.2	1.57	314.0	1.2
2000.0	0.0025	93.0	1.55	620.0	2.1

Experimental conditions: $m_{PS\text{-}IL\text{-}COOH}$= 100 mg, pH≈6, room temperature.

Table S4. Analytical performance of the proposed method in milk sample.

Parameter	Obtained values
Calibration curve	y=0.03056x+0.00231
R^2	0.9996
LOD (μg/mL)	0.003
LOQ (μg/mL)	0.01
Inter-day RSD, %	3.7
Intra-day RSD, %	2.9
Average Recovery, %	93±3

Table S5. Comparison for the extraction of DS by PS-IL-COOH and commercial adsorbents.

Adsorbent	$C_{initial\ DS}$=10 mg/L		$C_{initial\ DS}$=1000 mg/L	
	E%	q_e (mg/g)	E%	q_e (mg/g)
Activated carbon	44.0	4.40	39.71	397.08
Activated alumina	12.4	1.24	11.72	117.21
Silica gel	12.0	1.20	10.94	109.39
Artificial zeolite	4.70	0.47	2.63	26.33
Weak-base anion exchange	43.1	4.31	36.51	365.1
PS-IL-COOH (this work)	100	10	93.41	934.12

Experimental conditions: $m_{adsorbent}$=10 mg, $V_{initial\ DS}$=10 mL, t=30 min, pH≈6, room temperature.

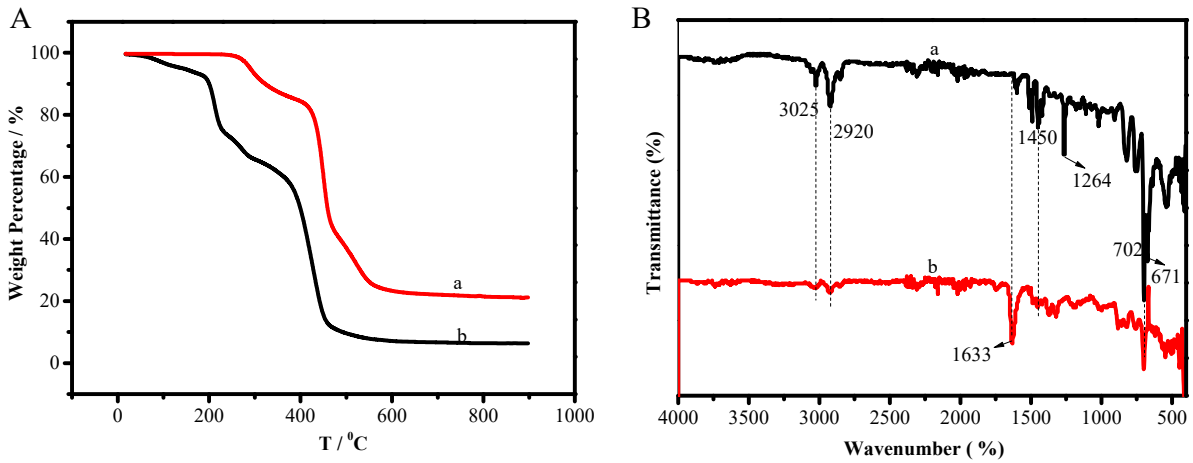

Figure S1. (A) The TGA curves of PS-CH_2Cl (a), and PS-IL-COOH (b); (B) FT-TR spectra of PS-CH_2Cl (a) and PS-IL-COOH (b).

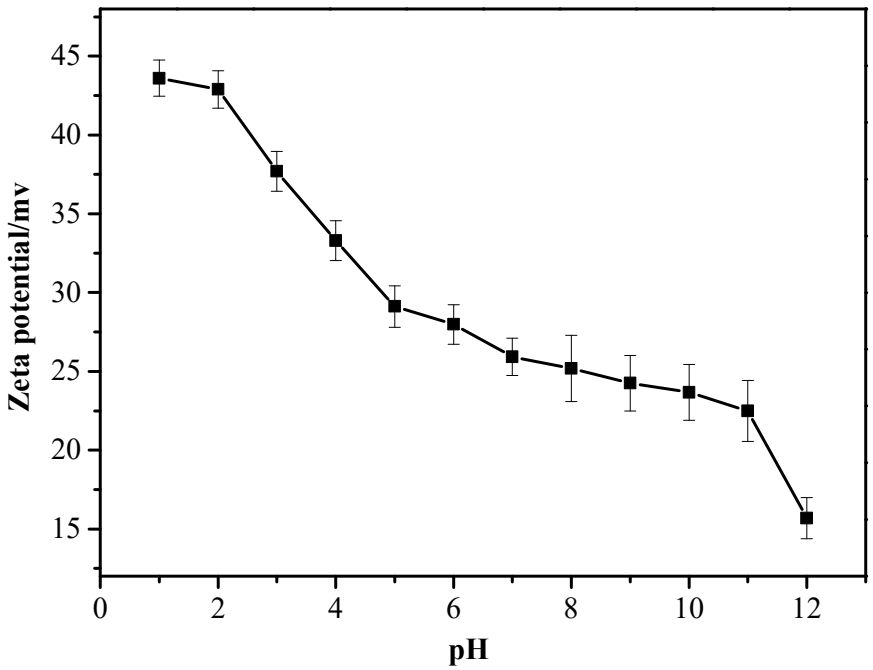

Figure S2. Zeta potential of PS-IL-COOH

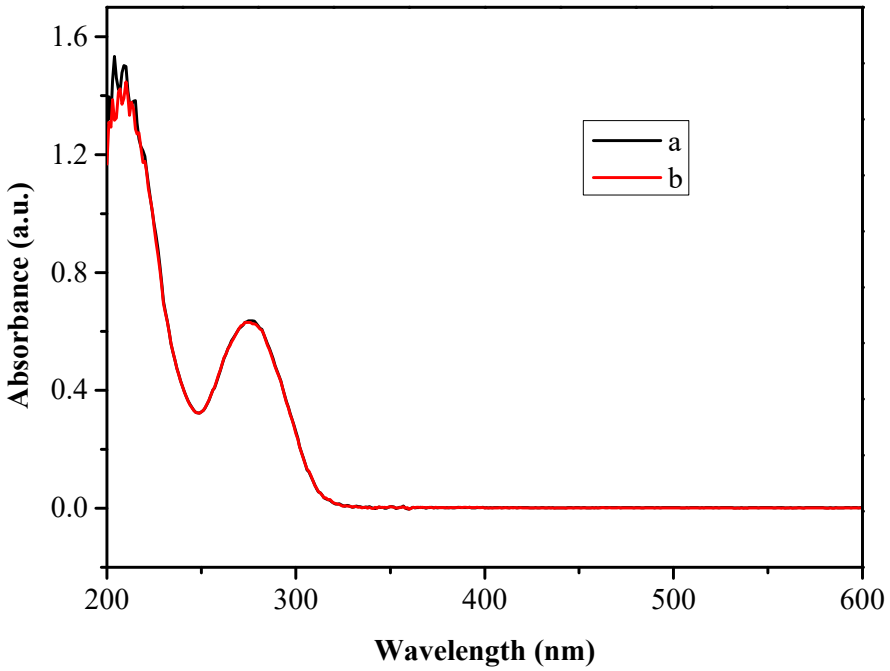

Figure S3. UV-visible adsorption spectra of the original DS (a) and the recovered DS (b).

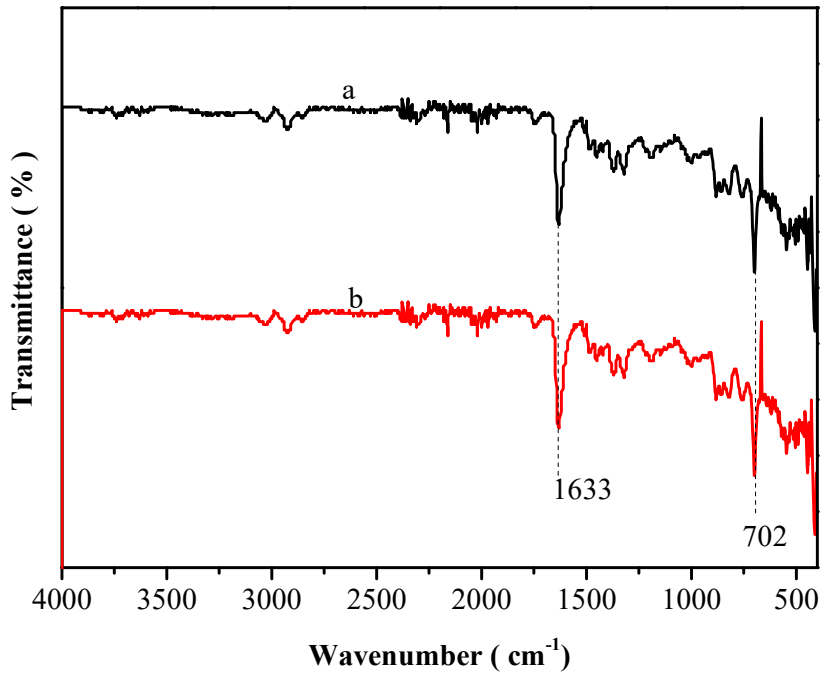

Figure S4. FT-IR spectra of the fresh PS-IL-COOH (a) and the regenerated PS-IL-COOH (b).

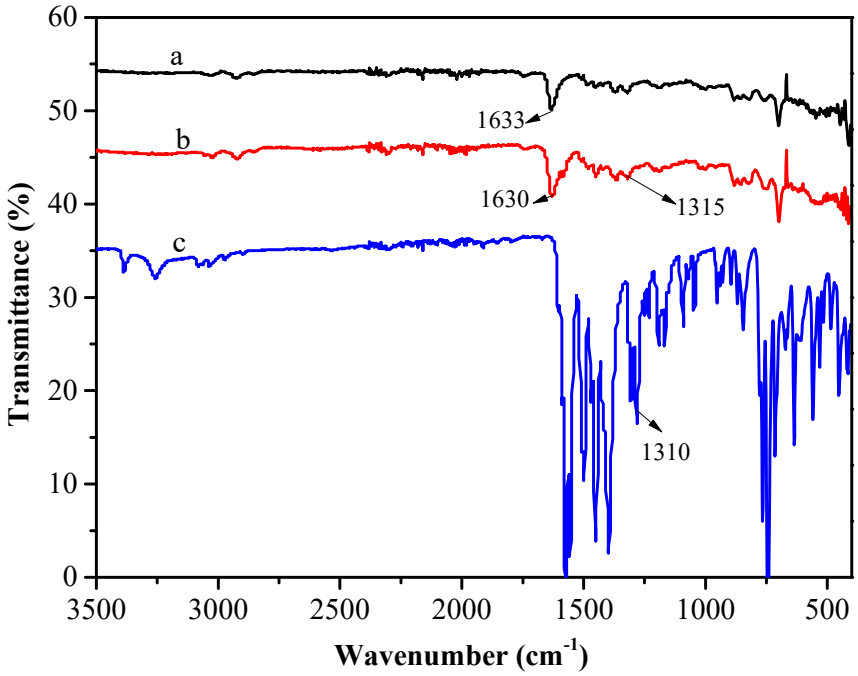

Figure S5. FT-IR spectra of the PS-IL-COOH (a), PS-IL-COOH-DS (b), and DS (c).

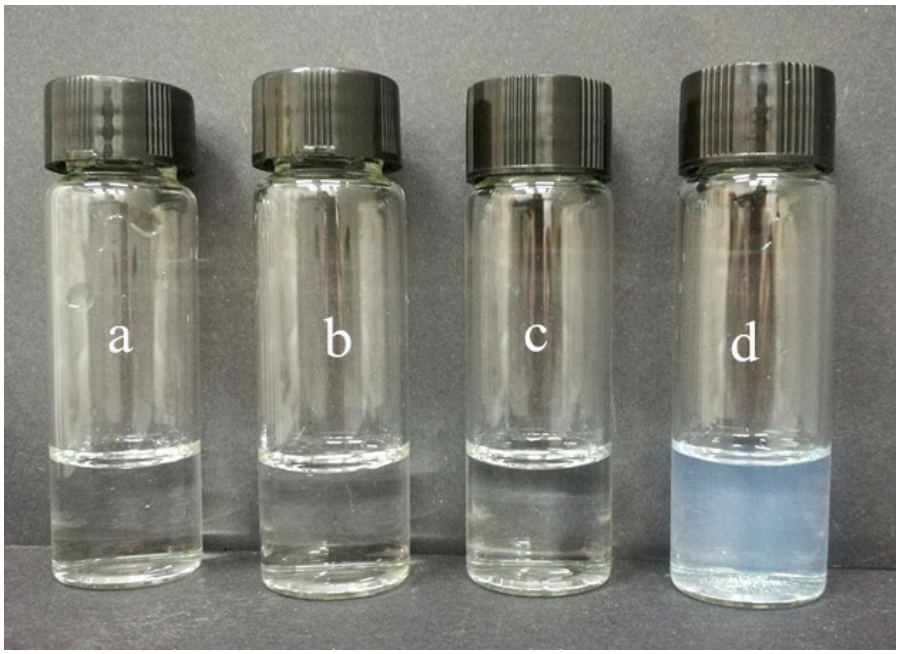

Figure S6. The photographs for different blank solutions and the adsorbed DS solution after addition of aqueous $AgNO_3$: (a) deionized water, (b) aqueous DS solution, (c) supernatant after soaking of PS-IL-COOH, (d) supernatant after DS was adsorbed by PS-IL-COOH. Experimental conditions: C_{DS}=100 mg/L, V_{DS}=5 mL, $m_{PS\text{-}IL\text{-}COOH}$=10 mg, time=30 min pH≈6, room temperature.