Electronic Supplementary Information

Metal organic framework/chitosan/polyethylene oxide composite columnar foam as sorbent for enrichment and detection of estrogens in environmental aqueous solutions

Huizhong Si[a], Pingping He[a], Xuemei Wang[a], Lin Li[a], Xiaohong Hou[b*]

[a]*School of Pharmacy, Shenyang Pharmaceutical University, Shenyang Liaoning Province, P. R. China*

[b]*School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang Liaoning Province, P. R. China*

[*]**Correspondence:** Professor Xiaohong Hou, School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang 110016, P. R. China
E-mail address: syphu_houxiaohong@163.com
Fax: **+86-24-43520212**

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1. Chemical structures of the four analytes

(a) (b)

(c) (d)

Fig. S1. Chemical structures of the four analytes. (A) Estradiol (E1), (B) Estradiol (E2), (C) Ethinyloestradiol (EE2), (D) Estriol (E3).

2. *Analytical conditions*

Shimadzu LC-20 A (Shimadzu, Japan) equipped with a fluorescence detector (FLD-20 A) were employed to conduct chromatographic separation and determination of E1, E2, EE2, E3 with a Diamonsil C18 analytical column (150 mm 4.6 mm i. d., 5 mm) from Dikma (Beijing, China). The mobile phase constituted of water (A) and acetonitrile (B) was set at a flow rate of 1 mL/min throughout the run. The gradient elution conditions were as follows: 0‑2 min, 35%‑60% B; 2‑9 min, 60% B; 9‑10 min, 60%‑100% B; 10-13 min, 100%-35% B. The injection volume was quantified as 20 μL, and the column temperature was kept constant at 30

3. N$_2$ adsorption-desorption isotherms of blank CS/PEO columnar foam
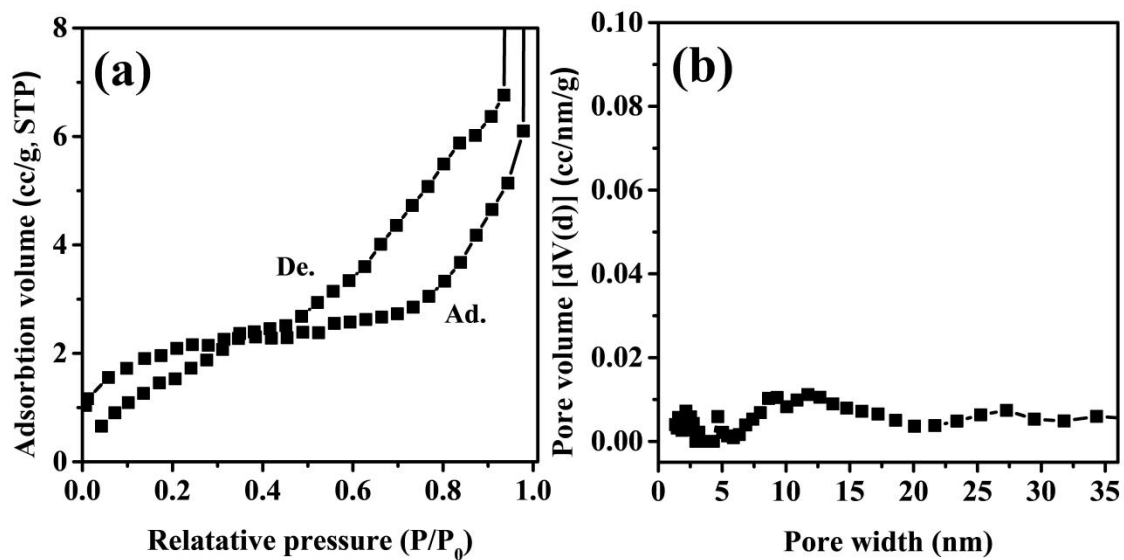
Fig. S2. N2 adsorption-desorption isotherms of the blank CS/PEO columnar foam. The BET surface area (a), the

pore size (b).

4. Effect of solution pH and ionic strength
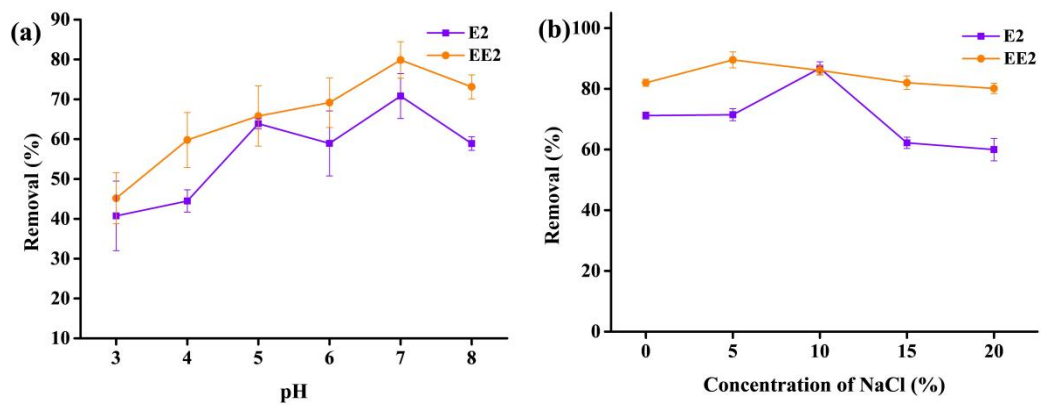
Fig. S3. Effect of pH (a), and ionic strength (b) on the removal of two estrogens by MIL-53(Al)/CS/PEO columnar foam.

5. Value of separation factor R_L of MIL-53(Al)/CS/PEO column foam towards two estrogens
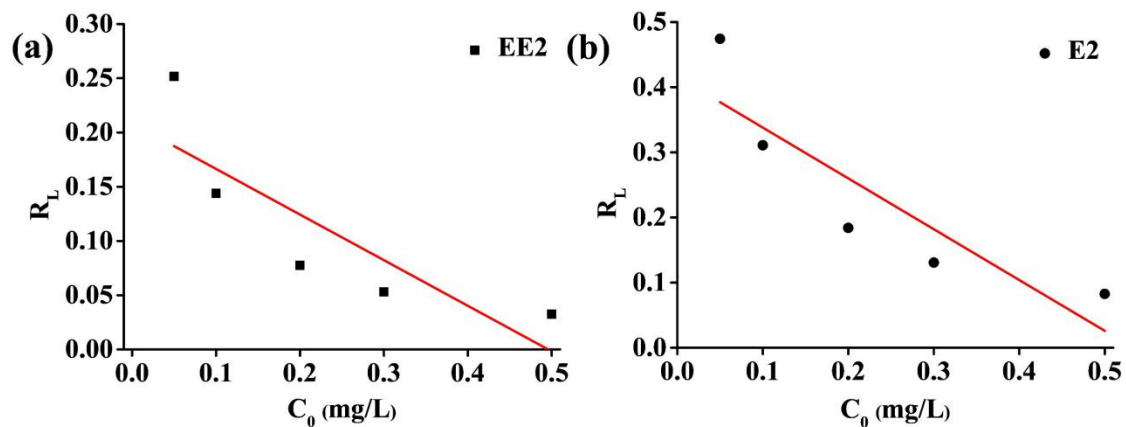
Fig.S4. Value of separation factor R_L of the adsorption of EE2 (a), and E2 (b) on MIL-53(Al)/CS/PEO column foam.

6. The plots of Langmuir and Temkin isotherm models for the adsorption of EE2 and E2 on

    MIL-53(Al)/CS/PEO columnar foam
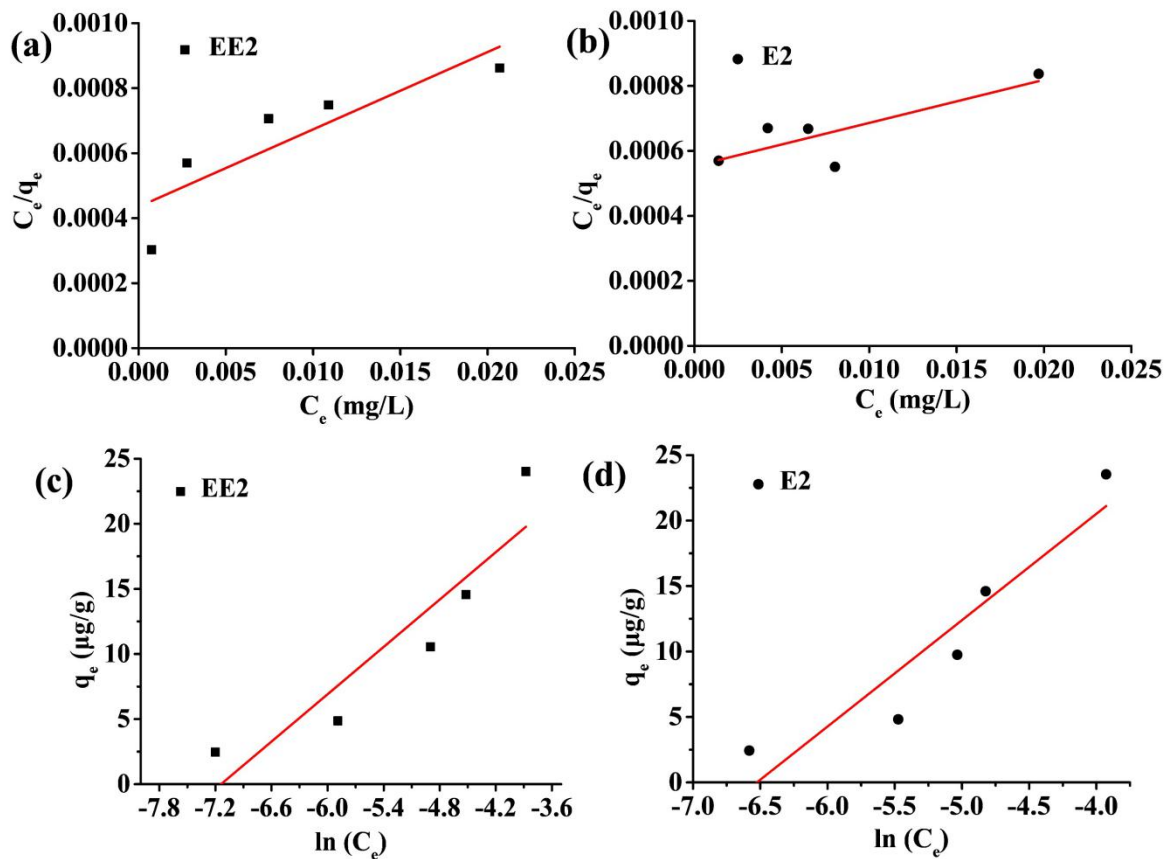
Fig. S5. The plots of Langmuir (a), (b) and Temkin isotherm (c), (d) models for the adsorption of EE2 and E2 on

MIL-53(Al)/CS/PEO columnar foam.

7. The van' Hoff plots of MIL-53(Al)/CS/PEO columnar foam towards two estrogens
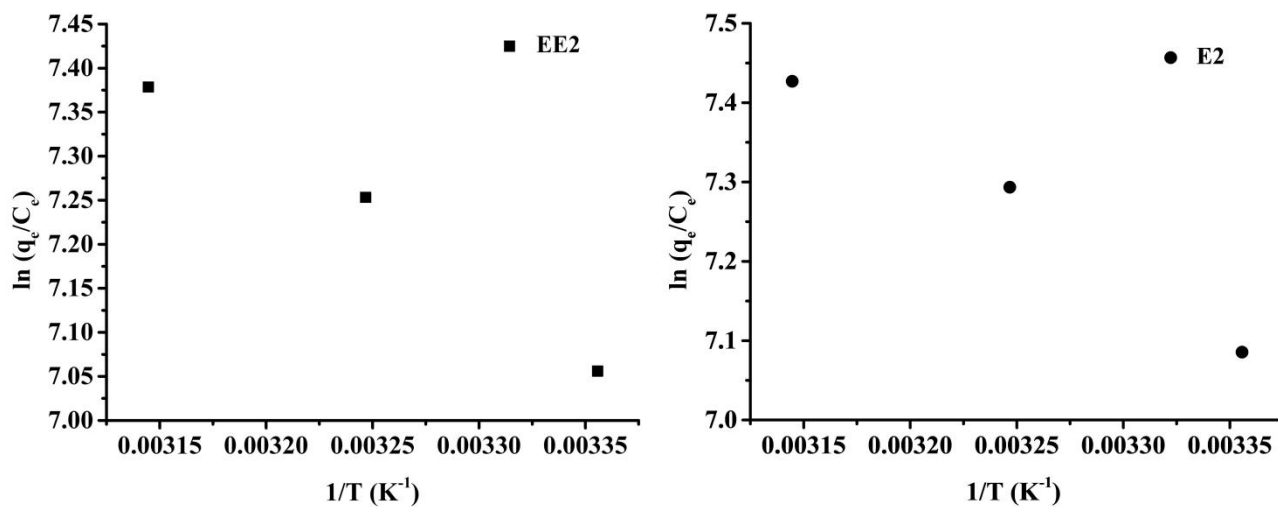
Fig.S6. The van' Hoff plots of MIL-53(Al)/CS/PEO columnar foam towards two estrogens.

8. Utilization durability of MIL-53(Al)/CS/PEO columnar foam
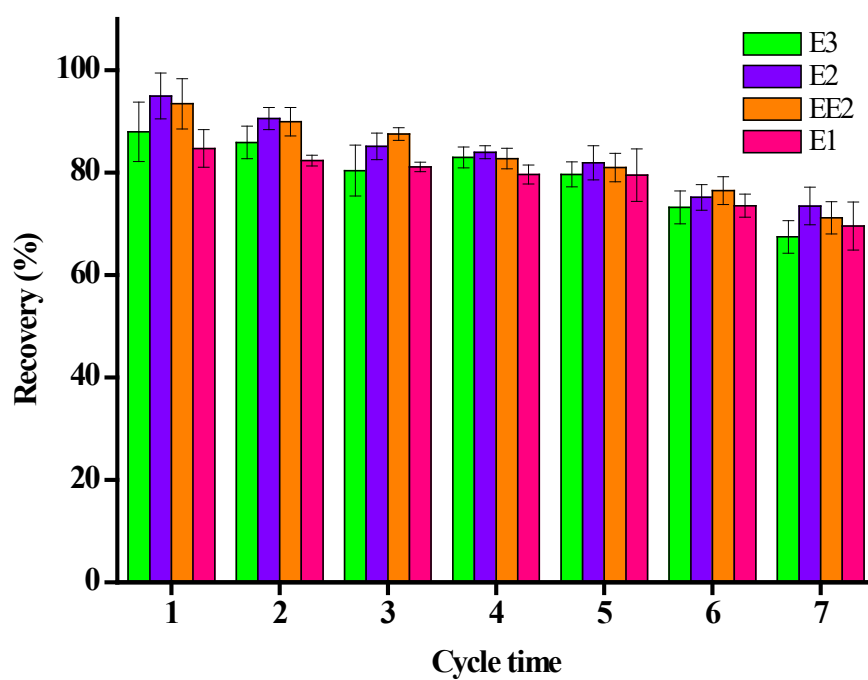
Fig. S7. Utilization durability of MIL-53(Al)/CS/PEO columnar foam in VA-SPE for the target analytes under the

optimal conditions.

9. The SEM photograph of clounmar foam after cycling five times
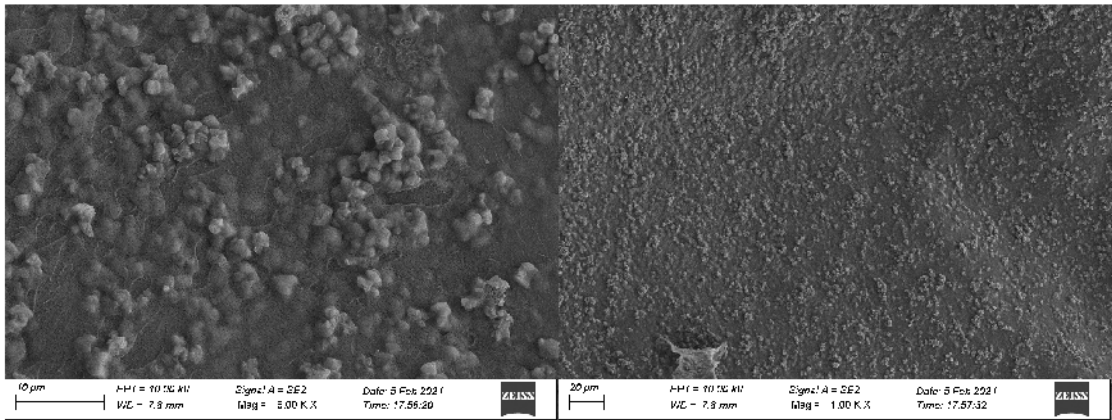
Fig. S8 The SEM photograph of clounmar foam after cycling five times

10. HPLC-FLD chromatograms of standard solution, spiked water sample and lake sample
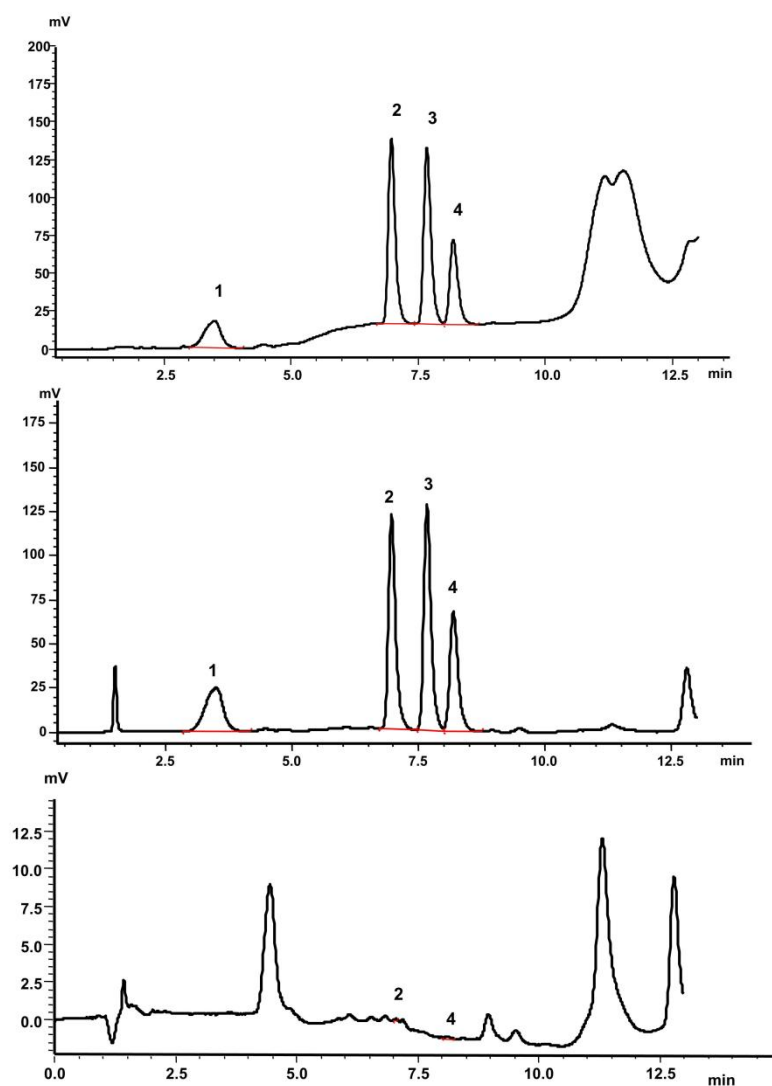
Fig. S9. HPLC-FLD chromatograms of standard solution, spiked water sample and lake sample. Peak identification:

(1) E3, (2) E2, (3) EE2, (4) E1.

11. Calibration curves of three estrogen solutions at different pH

The aqueous stock solution of E2 and EE2 (1 mg L^{-1}) were diluted by ultrapure water to prepare five standard solutions at concentration levels of 0.25, 1.0, 5.0, 20.0, 50.0, 100.0, 200.0 µg L^{-1}, respectively. Then, each estrogen solution was adjusted to pH value at 3, 4, 5, 6, 7, 8, and 9 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solution. The fluorescence intensities of estrogen solutions were measured using fluorospectrophotometer with the excitation and emission wavelengths of 280 nm and 310 nm, respectively. Calibration curves were constructed by the least squares linear regression analysis of the fluorescence intensity (*y*) versus the concentration (*x*).

Table S1. Calibration curves of EE2 and E2 at different pH.

| Analyte	pH	Linear range (µg L^{-1})	Standard curve equation	r^2
EE2	3	0.25-200	y = 111.09x - 49.44	0.9998
	4	0.25-200	y = 112.21x + 101.6	0.9999
	5	0.25-200	y = 113.98x + 59.818	0.9994
	6	0.25-200	y = 112.33x + 55.002	0.9997
	7	0.25-200	y = 112.17x + 90.372	0.9998
	8	0.25-200	y = 111.75x + 109.39	0.9999
E2	3	0.25-200	y = 108.49x - 41.054	0.9993
	4	0.25-200	y = 110.64x - 17.328	0.9995
	5	0.25-200	y = 108.62x + 8.9442	0.9999
	6	0.25-200	y = 109.08x + 34.55	1
	7	0.25-200	y = 108.74x + 30.452	0.9998
	8	0.25-200	y = 109.32x - 4.7402	0.9999

12. Thermodynamic parameters of the adsorption of EE2 and E2 on MIL-53(Al)/CS/PEO columnar foam

Table S2. Thermodynamic parameters of E2 and EE2 adsorption onto MIL-53(Al)/CS/PEO columnar foam.

Analyte	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
EE2	298	-17.48	12.71	101.40
	308	-18.57		
	318	-19.51		
E2	298	-17.55	13.48	104.22
	308	-18.68		
	318	-19.64		

13. Factors and levels of orthogonal experiments

Table S3. Factors and levels of the orthogonal experiments

Levels	Factors *			
	A	B	C	D
1	20	75	4:1	40
2	30	100	3:1	60
3	40	125	2:1	80

*A, the amount of MOFs (mg);

B, glutaraldehyde dosage (μL);

C, the proportions of CS/PEO (w/w);

D, acetic acid glacial dosage (μL)

14. Results analysis of the orthogonal experiments

Table S4. Result analysis of the orthogonal experiments

No.	Factors*				Recovery (%)
	A	B	C	D	
1	1	1	1	1	51.51
2	1	2	2	2	69.22
3	1	3	3	3	50.46
4	2	1	2	3	80.25
5	2	2	3	1	75.76
6	2	3	1	2	67.53
7	3	1	3	2	74.09
8	3	2	1	3	67.60
9	3	3	2	1	69.04
K1	171.19	205.85	186.64	196.31	
K2	223.54	212.58	218.51	210.84	
K3	210.73	187.03	200.31	198.31	
k1	57.06	68.62	62.21	65.44	
k2	74.51	70.86	72.84	70.28	
k3	70.24	62.34	66.77	66.10	
R	17.45	8.52	10.62	4.84	

*A, the amount of MOFs (mg);

B, glutaraldehyde dosage (μL);

C, the proportions of CS/PEO (w/w);

D, acetic acid glacial dosage (μL)

15. Linear ranges, correlation coefficients, limits of detection, limits of quantitative, precision, and repeatability for four analytes

Table S5. Linear ranges, correlation coefficients, limits of detection, limits of quantitative, precision, and repeatability for four analytes.

Analyte	Interday precision (RSD%, $n = 9$)			Intraday precision (RSD%, $n = 18$)			Repeatability (RSD%, $n = 6$)
	Low[a]	Middle[b]	High[c]	Low[a]	Middle[b]	High[c]	
E3	3.2	4.4	6.5	6.0	5.0	3.6	4.8
E2	4.0	2.7	2.9	11.3	4.2	3.5	4.0
EE2	5.3	3.3	2.6	7.0	1.6	2.1	3.0
E1	4.5	3.6	3.8	9.1	6.2	5.1	5.3

a: 0.04 ng mL^{-1} for E3, E2 and EE2, 0.4 ng mL^{-1} for E1

b: 0.5 ng mL^{-1} for E3, E2 and EE2, 5 ng mL^{-1} for E1

c: 3.0 ng mL-1 for E3, E2 and EE2, 30 ng mL-1 for E1

16. Uncertainty introduced by sample addition recovery

Table S6. Uncertainty introduced by sample addition recovery

Water sample	Recovery (RSD)%					Average (%)	S(R)	u(R)
	Sample1	Sample2	Sample3	Sample4	Sample5			
E3	104.8	100.9	104.6	104.2	110.7	105.0	3.5	1.6
E2	110.7	100.4	105.5	104.6	97.1	103.7	5.2	2.3
EE2	83.5	95.5	86.7	90.2	101.1	91.4	7.0	3.1
E1	93.3	96.3	99.0	94.6	101.7	97.0	3.4	1.5

17. Enrichment factor under different water sample

Table S7. Enrichment factors of estrogen in different water samples

Water sample	Enrichment factor			
	E3	E2	EE2	E1
Sample1	104.8	110.7	83.5	93.3
Sample2	100.9	100.4	95.5	96.3
Sample3	104.6	105.5	86.7	99.0
Sample4	104.2	104.6	90.2	94.6
Sample5	110.7	97.1	101.1	101.7