Electronic Supplementary Material (ESI) for RSC Advances.

Electric Supplementary Information (ESI) for

One-pot synthesis of magnetic molecularly imprinted microspheres by RAFT precipitation polymerization for fast and selective removal of 17β-estradiol

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Fig. S1. DTG curves of four particles.

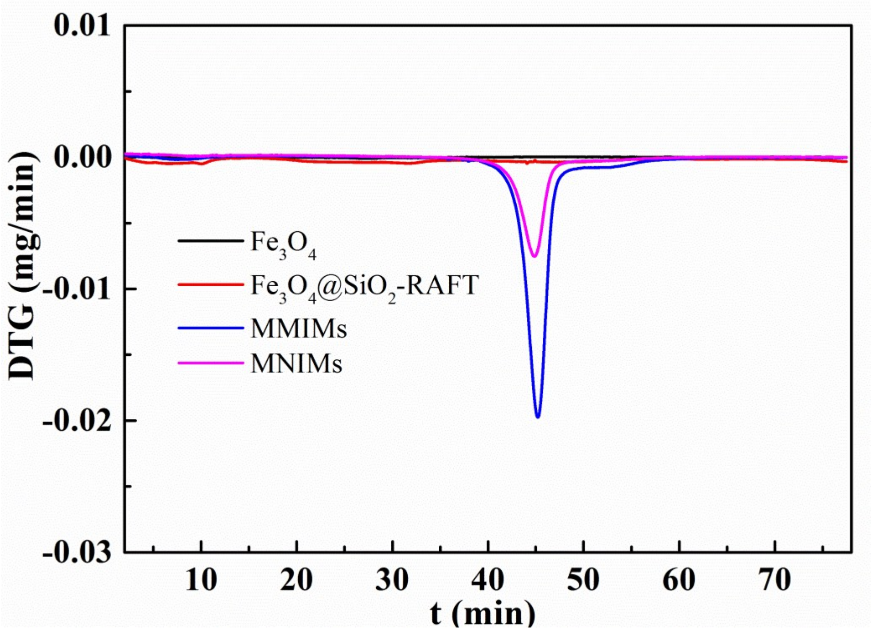

Fig. S2. HPLC-UV chromatograms of seawater, soil, yogurt and lake water samples without extraction (a), (c) and with MMIMs-MSPE extraction (b) (d). The samples were not spiked (a), (b) and spiked with 10 mg/L 17β-E2 (c), (d).

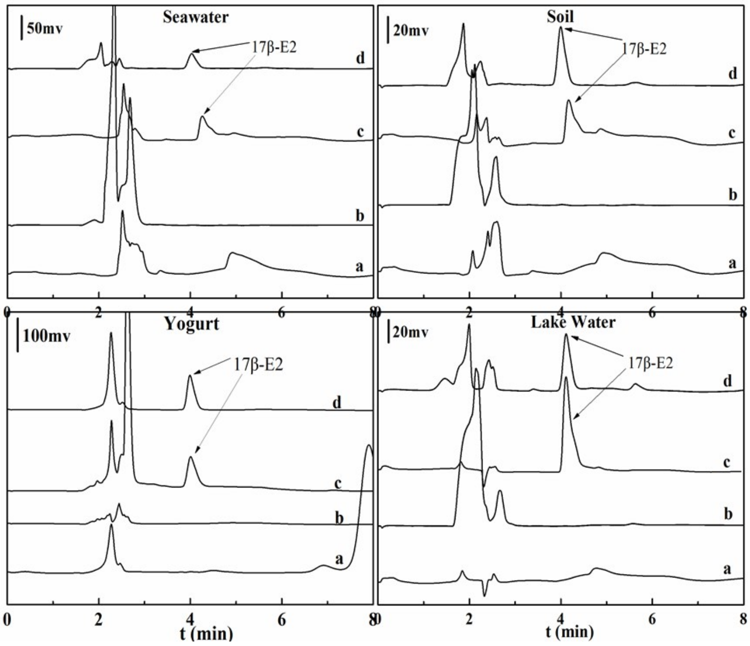

Table S1. TGA results of the five different particles.

Parameters	M_0 (mg)	ΔM (mg)	Residual (%)	Peak T (°C)	Peak V (mg/min)
Fe_3O_4	3.9680	0.037	99.06	/	/
Fe_3O_4@SiO_2	9.3270	0.62	93.33	365.24	0.10
Fe_3O_4@SiO_2-RAFT	6.7410	1.16	82.74	/	/
MMIMs	4.8760	3.63	25.61	454.36	1.16
MNIMs	2.3620	1.50	36.30	451.72	0.44

Table S2. Magnetization parameters.

Parameters	Coercivity (G)	M_s (emu/g) (a)	M_r (emu/g) (b)	B (c)
MMIMs	38.437	2.2788	0.11826	0.0519
MMIMs-Control	86.352	3.5021	0.33889	0.0968
MNIMs	21.758	3.0151	0.12815	0.0425

(a) M_s (magnetization saturation) is the terminal equilibrium magnetic intensity value of the magnetic hysteresis loop.

(b) M_r (Magnetization remanence) is the intersection point value between rising loop and the Y axis.

(c) B (M_r/M_s) reflects the relative magnetic induction intensity of the materials. The value of B is between 0 and 1: a large value represents stronger magnetic and wider magnetic hysteresis loop, like permanent magnet. On the contrary, small value means weaker magnetic and narrower magnetic hysteresis loop, like magnetic fluid.

Table S3. Specific surface area and other related data of MMIMs, MMIMs-Control and MNIMs obtained by BET analysis.

Parameters	Specific surface area (m^2/g)	Cumulative pore area (m^2/g)	Cumulative pore volume (mL/g)	Average pore diameter (nm)
MMIMs	444.8614	220.00	0.1006	4.18
MMIMs-Control	6.8897	14.11	0.0298	7.96
MNIMs	46.1846	48.15	0.0378	4.35

Table S4. Parameters obtained of 17β-E2 adsorption onto the polymers from four adsorption isotherm models.

Isotherm Models	Parameters	MMIMs	MMIMs-Control	MNIMs
Langmuir	R^2[a]	0.9990	0.9924	0.9911
$\{\frac{C_e}{q_e}=\frac{1}{q_{max}}C_e+\frac{1}{k_L q_{max}}\}$	$q_{\max}$[b]	0.787±0.011	0.735±0.030	0.215±0.009
	k_L[c]	0.125±0.012	0.042±0.004	0.066±0.010
Freundlich	R^2	0.9371	0.9778	0.9808
$\{lnq_e=\frac{1}{n}lnC_e+lnk_F\}$	k_F[d]	0.273±0.025	0.091±0.010	0.050±0.004
	$1/n$[e]	0.222±0.025	0.420±0.028	0.295±0.018
Redlich-Peterson	R^2	0.9990	0.9907	0.9922
$\{ln\left(q_{\max}a_R\frac{C_e}{q_e}-1\right)=b_R lnC_e+lna_R\}$	q_{max}	1.020±0.210	0.492±0.213	0.086±0.035
	a_R[f]	0.078±0.013	0.072±0.019	0.384±0.216
	b_R[g]	1.054±0.054	0.919±0.158	0.814±0.140
Langmuir-Freundlich	R^2	0.9995	0.9993	0.9998
$\{\frac{1}{B}=\frac{1}{N_t a}(\frac{1}{F})^m+\frac{1}{N_t}\}$	N_t[h]	212.8±63.75	∞	185.2±107.8
	α ($*10^{-4}$)[i]	5.677±0.572	1/∞	2.878±0.180
	m[j]	2.075±0.068	1.963±0.038	1.323±0.032

[a] Correlation coefficient.

[b] Maximum absorption capacity.

[c] Langmuir constant.

[d] Freundlich constant.

[e] Related to adsorption intensity and surface heterogeneity.

[f] Redlich-Peterson isotherm constant.

[g] Redlich-Peterson isotherm exponent.

[h] Total number of binding sites.

[i] Related to the median binding affinity constant K_0 via $K_0 = \alpha^{1/m}$.

[j] Heterogeneity index, ranging from 0 to 1, be equal to 1 for homogeneous materials.

Table S5. Parameters obtained of 17β-E2 adsorption towards the MMIMs from four kinetic adsorption models.

Kinetic Models	Parameters		
Pseudo-first-order	k_1 (min^{-1})a)	q_e (mg/g)b)	R^2c)
{ $ln(q_e - q_t) = lnq_e - k_1 t$ }	0.031±0.006	0.649±0.032	0.9478
Pseudo-second-order	k_2 (g/(mg·min))d)	q_e (mg/g)	R^2
{ $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ }	0.049±0.005	0.764±0.018	0.9966
Elovich	α (mg/g)e)	β (min·g/mg)f)	R^2
{ $q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t)$ }	0.114±0.013	7.798±0.212	0.9945
Intraparticle diffusion	k_{id} (mg/(g min$^{0.5}$))g)	C (mg/g)h)	R^2
{ $q_t = k_{id} t^{1/2} + C$ }	0.045±0.002	0.140±0.014	0.9941
	0.015±0.001	0.460±0.002	0.9999

a) Rate constant of adsorption in pseudo-first-order model.

b) Saturated adsorption amount of template molecule at equilibrium.

c) Correlation coefficient.

d) Rate constant of adsorption in pseudo-second-order model.

e) Initial adsorption rate constant.

f) Desorption constant.

g) Intraparticle diffusion rate constant, which relates to the particle size R through the equation: $k_p = \frac{6Q_e}{R}\sqrt{\frac{D}{\pi}}$.

h) Constant provides information about the thickness of the boundary layer.

1. Adsorption isotherms fitting

The relationships between adsorbent and adsorbate described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium, can be described by adsorption isotherms. There are four types of isotherms. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$q_e = \frac{k_{\mathrm{L}} q_{\max} C_e}{1 + k_{\mathrm{L}} C_e} \quad \left(\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{k_{\mathrm{L}} q_{max}} \right) \qquad (1)$$

Where， q_e (mg/g) is the amount of template molecule adsorbed by per unit weight of sorbent at equilibrium under different initial concentrations, C_e (mg/L) is the initial concentration of template molecule in the solution, q_{max} (mg/g) is the theoretical maximum adsorption at monolayer coverage under fixed conditions, and k_L (L/mg) is the adsorption equilibrium constant which is related to energy of adsorption, which heat of adsorption of template molecule can be calculated from the temperature dependence of the equilibrium adsorption constant k_L via the Clausius-Claperyon's equation $\{\partial log k_L / \partial (1/T) = -\triangle H / 2.303R\}$.

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$q_e = k_F C_e^{1/n} \quad \left(ln q_e = \frac{1}{n} ln C_e + ln k_F \right) \qquad (2)$$

Where, q_e and C_e have the same definitions in equation (1), k_F (mg/g)(L/mg)^n is a Freundlich constant indicating the adsorption capacity, and 1/n is a constant depicting the adsorption intensity or surface heterogeneity, ranging from 0 to 1.

The above models described isotherms with two parameters but Redlich-Peterson model describes three-parameter isotherm, and its non-linear equation is expressed as:

$$q_e = \frac{q_{\max} a_{\mathrm{R}} C_e}{1 + a_{\mathrm{R}} C_e^{b_{\mathrm{R}}}} \quad \left(q_{\max} a_{\mathrm{R}} \frac{C_e}{q_e} = a_R C_e^{b_{\mathrm{R}}} + 1 \right) \qquad (3)$$

Where, q_e, q_{max} and C_e have the same definitions in equation (1), a_R (L/mg) is the Redlich-Peterson isotherm constant, b_R is the Redlich-Peterson isotherm exponent. At low concentrations, the Redlich-Peterson isotherm approximates to Henry's law and at high

concentration its behavior approaches to the Freundlich isotherm.
The Langmuir-Freundlich non-linear equation is established as:

$$B = \frac{N_t \alpha F^m}{1 + \alpha F^m} \quad \{\frac{1}{B} = \frac{1}{N_t \alpha}(\frac{1}{F})^m + \frac{1}{N_t}\} \qquad (4)$$

where, B and F (L/mg) represent the concentrations of bound and free template molecules, respectively, N_t (mg/g) is the total number of binding sites, α (g/mg) is related to the median binding affinity constant K_0 *via* $K_0 = \alpha^{1/m}$, and m is the heterogeneity index which can be equal to 1 for a homogeneous material, or will take values within 0 and 1 if the material is heterogeneous.

2. Kinetics fitting

The dynamic binding was further investigated by four kinetic models. The pseudo-first-order equation is given as follow:

$$ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

where, q_t (mg/L) is the instantaneous concentration of template molecule adsorbed on the surface of per unit weight of sorbent at time t in the adsorption process, q_e (mg/L) is the saturated adsorption amount of template molecule at equilibrium under certain conditions, k_1 is the adsorption rate constant of pseudo-first-order model.
The pseudo-second-order equation is given as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where, q_t (mg/L) and q_e (mg/L) have the same definitions with pseudo-first-order model, k_2 is the adsorption rate constant of pseudo-second-order model.
The Elovich equation can be expressed as:

$$q_t = \frac{1}{\beta} ln(a\beta) + \frac{1}{\beta} ln(t) \qquad (7)$$

where, q_t (mg/L) is the same definition with pseudo-first-order model, α and β represent the initial adsorption rate constant and desorption constant, respectively.

The intraparticle diffusion equation can be expressed as:

$$q_t = k_{id} t^{1/2} + C \qquad (8)$$

where, q_t (mg/L) is the same definition with pseudo-first-order model, k_{id} is the intraparticle diffusion rate constant and C is a constant revealed the thickness of the boundary layer.

References

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