Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 285–286

Magnetic sorbent modified by humate for the extraction of alkylphenols, bisphenol A and estradiol

Alexander S. Gubin, Pavel T. Sukhanov and Aleksei A. Kushnir

Instruments and reagents. Nonylphenol (technical-grade mixture, HPLC/GC standard, >95% purity, Supelco), 4-octylphenol (>99% purity, Supelco), 17β-estradiol acetate (>99% purity, Merck), and bisphenol A (analytical standard, 100 mg, Supelco) were used. Fe_3O_4 were synthesized using $FeCl_3\cdot 6H_2O$ (≥98.0%, Merck), $FeSO_4\cdot 7H_2O$ (99.9%, Lenreaktiv, Russia), and $NH_3\cdot H_2O$ (Lenreaktiv, Russia). Sorbents were synthesized using tetraethyl orthosilicate (TEOS, 99% purity, Acros Organics), sodium citrate (reagent grade, ($C_6H_5Na_3O_7\cdot 5.5H_2O$, Lenreaktiv, Russia), dimethylformamide (reagent grade, Ekos-1, Russia), and thionyl chloride (at least 99.5% of the main substance, Acros Organics). Desorption was carried out using methanol (99.8%, Lenreaktiv, Russia).

The magnetic sorbent was synthesized using an ES8300 overhead stirrer (EKROSKHIM, Russia). The reaction mixture was heated and cooled using a RE 415 GLCK 1911 thermostat (LAUDA, Germany). Ultrasonic treatment of the reaction mixture was carried out in a Branson B1510 ultrasonic bath. Functional groups on the sorbent surface were identified by IR spectroscopy (InfraLum FT-08, Lumex, Russia). The specific surface area of the sorbent (S, $m^2\ g^{-1}$) was determined by BET. The nanoparticle morphology was determined using a JSM-6510LV scanning electron microscope (Jeol, Japan) and a Libra 120 transmission electron microscope (Carl Zeiss, Germany). XRD spectra were obtained on an ARL X'TRA diffractometer (Thermo Scientific, Switzerland). The magnetic characteristics of the nanosorbent were studied using a VSM-7410S magnetometer (Lake Shore, United States). The solution pH was controlled using a pH-150M meter (Akvilon, Russia). The qualitative analysis of the samples was carried out by GC-MS on an Agilent 7890B GC system with an Agilent 5977A MSD mass selective detector.

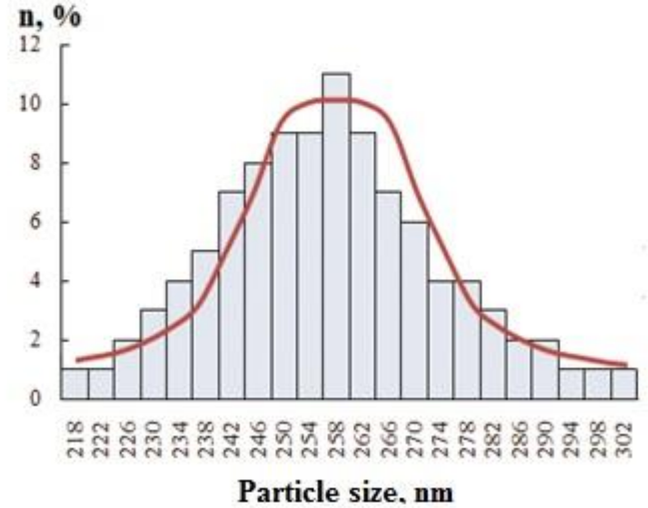

Figure S1. Particle size distribution for the $Fe_3O_4@SiO_2$-HA sorbent.

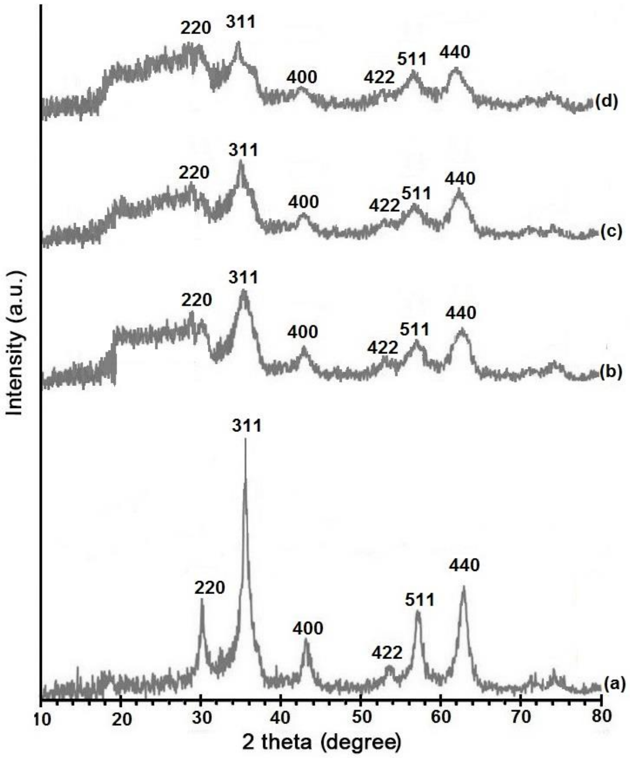

Figure S2. XRD pattern for (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$, (c) $Fe_3O_4@SiO_2$-NH_2, and (d) $Fe_3O_4@SiO_2$-HA.

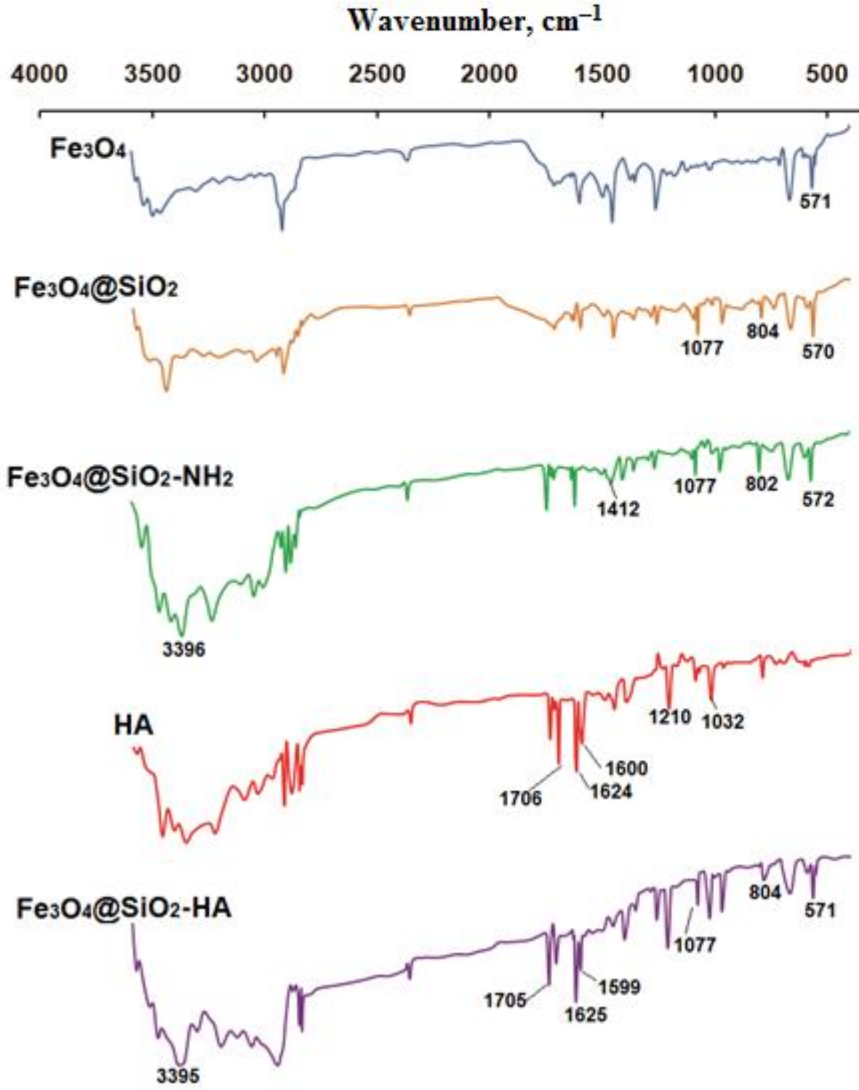

Figure S3. FT-IR spectra for magnetite (Fe_3O_4); silica-coated Fe_3O_4 nanoparticles ($Fe_3O_4@SiO_2$); silica-coated Fe_3O_4 nanoparticles modified with amino groups ($Fe_3O_4@SiO_2$-NH_2); free humic acids (HA) and Fe_3O_4 nanoparticles modified with humates ($Fe_3O_4@SiO_2$-HA).

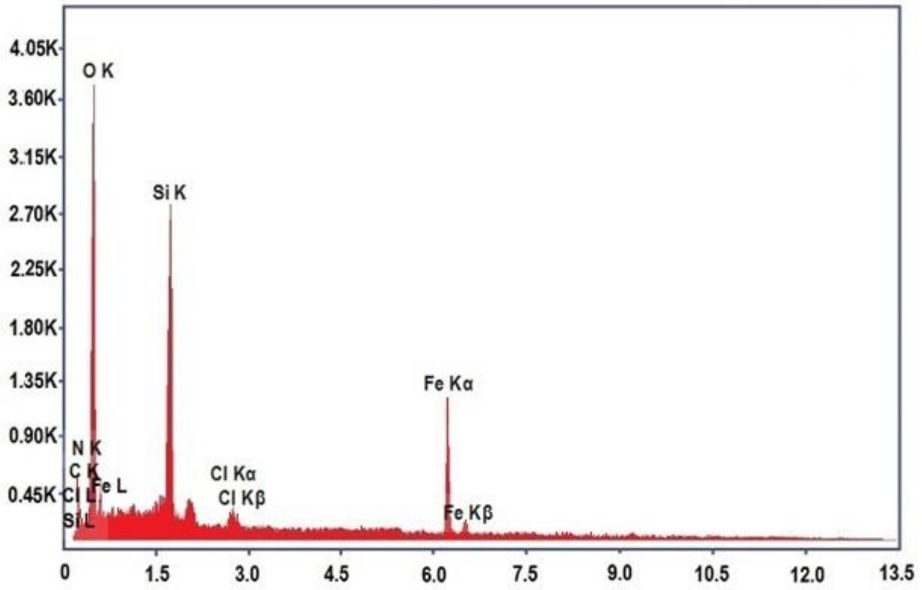

Figure S4. Elemental analysis (EDS spectrum) for the $Fe_3O_4@SiO_2$-HA sorbent

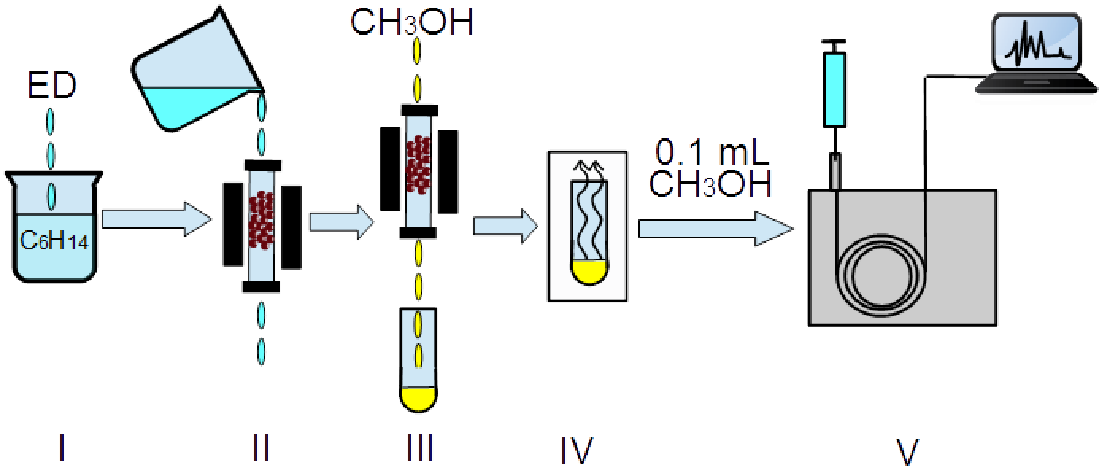

Figure S5. Scheme of enrichment experiment using the $Fe_3O_4@SiO_2$-HA magnetic sorbent: (I) addition of ED to a hexane solution; (II) passing of the hexane solution of ED through a column with $Fe_3O_4@SiO_2$-HA; (III) desorption with methanol; (IV) evaporation in the stream of nitrogen; and (V) GC-MS determination of ED.

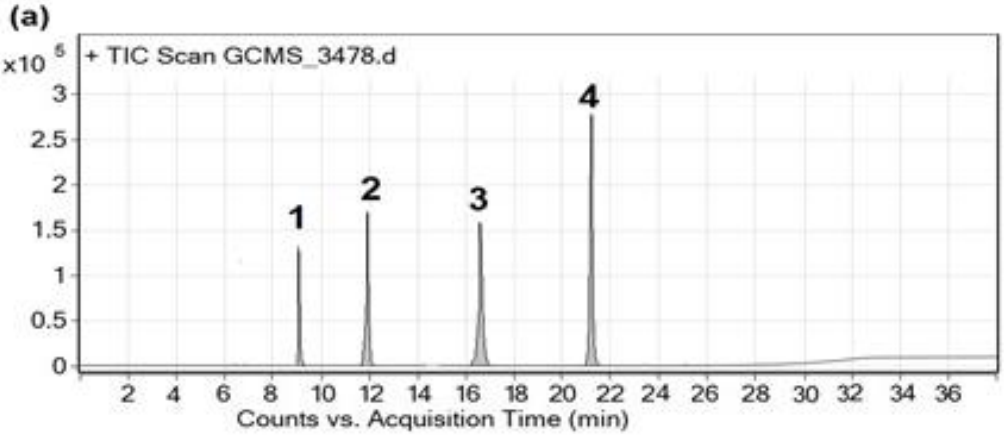

Figure S6. Chromatograms for separation of ED mixtures (the number in parentheses are peak numbers): 4-OP (1), 4-NP (2), BPA (3), and E2 (4). Chromatography conditions: Agilent 7890B GC system with Agilent 5977A MSD; sample injection (1.0 μL), split ratio 30:1; HP-5MS UI nonpolar column (30 m × 0.250 mm × 0.25 μm); the stationary phase was 5% (phenyl)-methylpolysiloxane; the carrier gas was helium (1.0 mL/min); the injection temperature was 300°C; the MSD temperature was 250°C; temperature programming: the starting temperature 150 °C was kept for 2 min, the temperature was increased at a rate of 10 °C/min to 280 °C and maintained for about 20 min; electron impact with radiation energy of 70 eV.

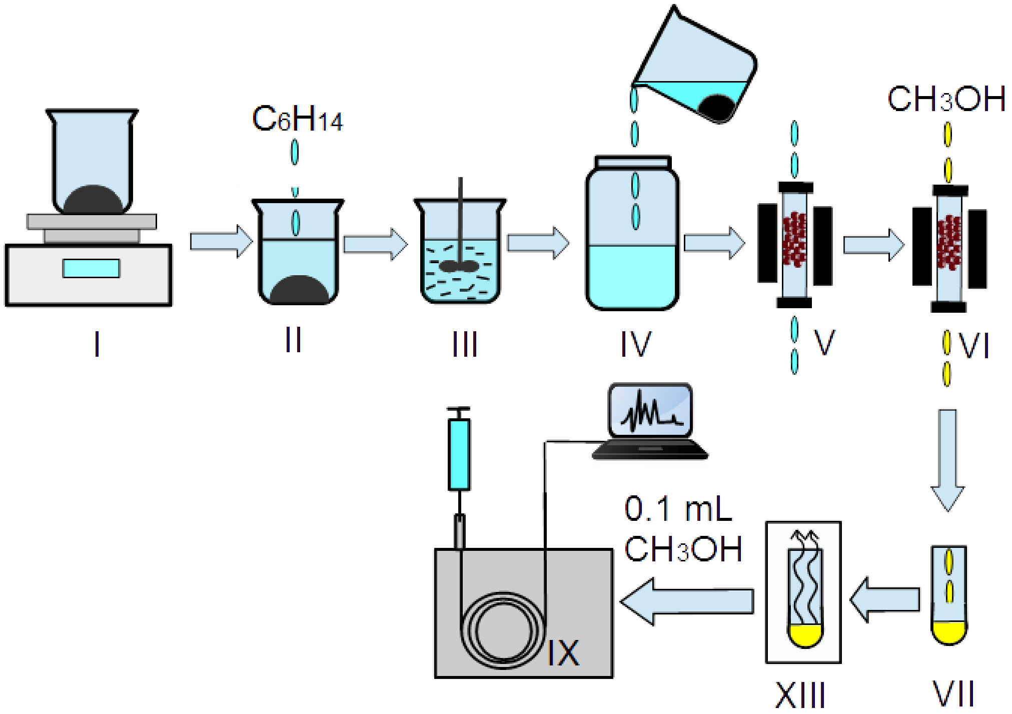

Figure S7. Scheme for analysis of the model sample of bottom sediments: (I) weighing of the sample (100 g); (II) addition of hexane; (III) stirring for 2 h; (IV) separation of bottom sediments from the hexane extract; (V) passing through a column with $Fe_3O_4@SiO_2$-HA; (VI) desorption with methanol; (VII) collection of the methanol extract; (VIII) evaporation to 0.1 mL; and (IX) injection to the chromatograph. ED was added after step IV.

Table S1. Analytical performances for the MSPE-GC-MS determination of EDs in bottom sediments after extraction with hexane

Substance	Added, ng/kg	Found, ng/kg	RR[a], %	Intraday precision[e], %	Interday precision[e], %	R^2	LOD[b], ng/kg	LOQ[c], ng/kg	Linearity[d], ng/kg
4-OP	0	-	-	-	-	0.998	1.0	3.0	3.0-800
	10	8.7	87	8.1	11.0				
	50	45	90	6.2	7.8				
	100	94	94	5.1	6.0				
	500	478	96	3.2	4.9				
4-NP	0	-	-	-	-	0.999	0.9	3.0	3.0-900
	10	8.4	84	7.8	11.6				
	50	46	92	4.9	8.2				
	100	95	95	4.3	5.3				
	500	481	97	2.4	3.5				
BPA	0	-	-	-	-	0.997	1.6	5.0	5.0-500
	10	9.5	95	6.4	9.9				
	50	49	98	5.7	7.8				
	100	102	102	4.5	5.1				
	500	525	105	2.1	3.3				
E2	0	-	-	-	-	0.998	1.8	6.0	6.0-900
	10	8,5	85	9,3	12,5				
	50	43	87	7,8	8,9				
	100	90	90	5,3	6,2				
	500	476	95	3,7	5,0				

*) Below limit of detection

[a] Relative recovery (n=6). [b] Limit of detection (S/N=3). [c] Limit of quantification (S/N=10). [d] Linearity range (n=6). [e] Relative standard deviation for intraday (n=3) and interday (n=6) precision.

Table S2. Analytical performances for the determination of ED in real bottom sediments (check of trueness by the spiking method)*

Substance	Added, ng/kg	Found, ng/kg	RR, %	Intraday precision, %[a]	Interday precision, %[a]
4-OP	-	287	-	4.0	7.0
	200	449	92	3.2	5.9
4-NP	-	332	-	3.3	6.8
	300	599	95	2.9	5.6
BPA	-	238	-	4.7	6.1
	200	457	104	3.6	4.9
E2	-	100	-	7.0	10.5
	300	370	93	4.7	7.8

*) Samples were analyzed as shown in Fig. S6

[a] Relative standard deviation for intraday (n=3) and interday (n=6) precision.

Table S3. Proposed method *vs.* known methods of solid-phase extraction (SPE) and magnetic solid-phase extraction (MSPE) of bisphenol A, 4-octylphenol, 4-nonylphenol, and 17β-estradiol

Analyte	Sorbent	Analysis method	*EF*	Sorption capacity, mg g^{-1}	Ref.
4-OP 4-NLP BPA E2	Fe_3O_4@SiO_2-HA	MSPE-GC-MS	1550 1618 1782 1815	740 809 895 1022	This method
BPA 4-OP 4-NP	Fe@MgAl-LDH	SPE-HPLC-VWD	300	–	S1
4-OP BPA	Molecularly imprinted polymers based on CdTe/CdS quantum dots, magnetic Fe_3O_4 and graphene oxide	SPE- UPLC	510	–	S2
4-NP BPA	Magnetic Fe_3O_4 dummy molecularly imprinted polymers based on multi-walled carbon nanotubes	MSPE-HPLC-UV	–	31.05 10.6	S3
BPA 4-OP 4-NP	Fe_3O_4@MON-NH_2	MSPE-HPLC-UV	197 196 192	824.1 116.6 117.9	S4
BPA	Magnetic Fe_3O_4 molecularly imprinted polymer	SPE-UV	–	40	S5
E2	Magnetic nanoparticles of graphene oxide (GO)/γ-Fe_2O_3	SPE-HPLC-FD	91	–	S6

References

S1. Q. Zhou, M. Lei, J. Li, K. Zhao and Y. Liu, *Sep. Purif. Technol.*, 2017, **182**, 78.

S2. S. Han, X. Li, Y. Wang and S. Chen, *Chem. Eng. J.*, 2015, **271**, 87.

S3. W. Rao, R. Cai, Y. Yin, F. Long and Z. Zhang, *Talanta*, 2014, **128**, 170.

S4. Z.-D. Du, Y.-Y. Cui, C.-X. Yang and X.-P. Yan, *Talanta*, 2020, **206**,120179.

S5. A. Karrat and A. Amine, *Microchem. J.*, 2021, **168**, 106496.

S6. F. N. Ferreira, A. P. Benevides, D. V. Cesar, A. S. Luna and J. S. de Gois, *Microchem. J.*, 2020, **57**, 104947.