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Supplementary material

Bioaccumulation investigation of bisphenol A in HepG2 cells and zebrafishes enabled by cobalt magnetic polystyrene microspheres derived carbon based magnetic solid-phase extraction

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1. Reagents and materials

Styrene (ST) was purchased from ChengDu Chron Chemicals Co., Ltd. (Chengdu, China). Ammonium hydroxide, tetraethoxysilane (TEOS) were provided by Xilong Scientific Co., Ltd. (Shenzhen, China). Oleic acid (OA) was obtained from Yantai Shuangshuang chemical Co., Ltd. (Yantai, China). Sodium dodecyl sulfate (SDS) was purchased from Beijing Donghuan United Chemical Factory (Beijing, China). Acrylic acid, n-hexane and anhydrous ethanol were gained from Damao Chemical Reagent

Factory (Tianjin, China). Azodiisobutyronitrile and bisphenol A were provided from Innochen Co., Ltd. (Beijing, China). Divinylbenzene was obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH) and ammonia were obtained from Sichuan Xilong Chemical Industry Co., Ltd. (Chengdu, China). Magnetic Co Nanoparticles were provided from Shanghai Shuitian Material Technology Co., Ltd. (Chengdu, China). Acetonitrile and Methanol were purchased from Yuwang Chemical (Shandong, China) and were of chromatographic grade. Ultra-pure water from a Millipore Direct-Q purification system (18.2 MΩ) was used throughout. HepG2 cells were purchased from the cell bank of Chinese Academy of Sciences, (China, http://www.cellbank.org.cn/). Newborn calf serum was supplied by Lanzhou Minhai Biological Engineering Co., Ltd (Lanzhou, China). Penicillin, and streptomycin were obtained from Hyclone (American, http://www.gelifesciences.com.cn/CNLS/jsp/Brand/Hyclone.html). Phosphate buffer solution (PBS, 0.01M) and cell lysate were provided by Beyotime Biotechnology (Shanghai, China). Cell counting Kit-8 (CCK-8) was supplied by Biosharp (Guangzhou, China). Zebrafishes were purchased from local fish market (Lanzhou, China). Other used chemicals were analytical grade without further purification. 4,4′-(Hexafluoroisopropylidene)diphenol (Bisphenol AF, BPAF) and 4,4′-(1-Phenylethylidene)bisphenol (bisphenol AP, BPAP) were purchased from Aladdin Industrial Corporation (Shanghai, China). 4,4'-Methylenediphenol (Bisphenol F, BPF) was supplied by Adamas Reagent, Ltd. (Shanghai, China).

2. Apparatus

The morphology of as-prepared adsorbents were analyzed by the field-emission scanning electron microscope (FESEM, Hitachi S4800). The FI-IR spectra were collected from Fourier transform infrared spectrometer (FTIR, Nexus 870, USA). X-rays photoelectron spectroscopy (XPS, Perkin-ElmerPHI-5702) with 1486.6 eV radiation as the excitation source was adopted for the surface chemical compositions characterization. The TGA curves were carried out on a thermal gravimetric analyzer

(STA449C, Germany) over a temperature range from 23 ºC to 800 ºC at a heating rate of 10 (K/min) under N_2 atmosphere. The nitrogen adsorption-desorption isotherm measurement was conducted at 77 K using Micrometrics ASAP 2020 HD88 for micropore structure analysis. Lake Shore 7304 vibrating sample magnetometer (VSM) (Lake-shore, USA) was conducted to investigated the magnetic property of the as-prepared materials. X-ray diffraction (XRD) data was collected from a Panalytical X'Pert Pro using CuKα radiation. The Raman spectra was obtained by Raman spectroscope (JY-HR800, the excitation wavelength of 532 nm). Z1 Cell Counter (Beckman) was used to calculate the cell numbers. Sonic oscillator was performed on Ultrasonic Cell Disrupter System (America, SONICS).

3. Chromatographic conditions

The BPA analysis was performed by an Agilent 1100 Series modular HPLC system with a 20 μL sample loop and a fluorescent detector (FLD) (Agilent Technologies, USA). C18 column (Hypersil ODS2, 250 mm length × 4.6 mm i.d., 5 μm) was used for the sample separation at 25 ºC and the flow rate was 1.0 mL min^{-1}. The volume ratio of mobile phase A (methanol) to B (0.02 M ammonium acetate solution) was 7:3. BPA was detected using FLD at an excitation wavelength (λ_{Ex}) of 275 nm and an emission wavelength (λ_{Em}) of 305 nm.

4. Comparison of extraction recovery of BPA and its analogues

BPAF, BPAP and BPF were dissolved in DMSO, and then diluted to 200 μg L^{-1} with PBS solution. Under aforementioned optimum conditions, the extraction performance of C-Co@PST for four bisphenols was investigated by extracting 1mL of standard solutions. The analytes analysis was performed by HPLC with a UV–vis detector. The detection wavelength was set at 210 nm. [S1]

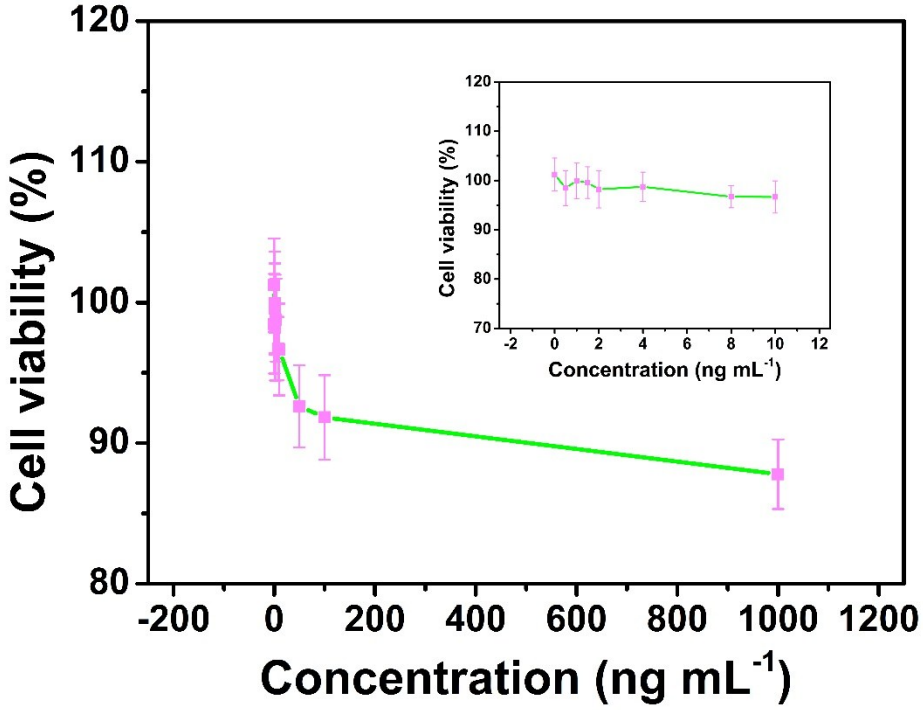
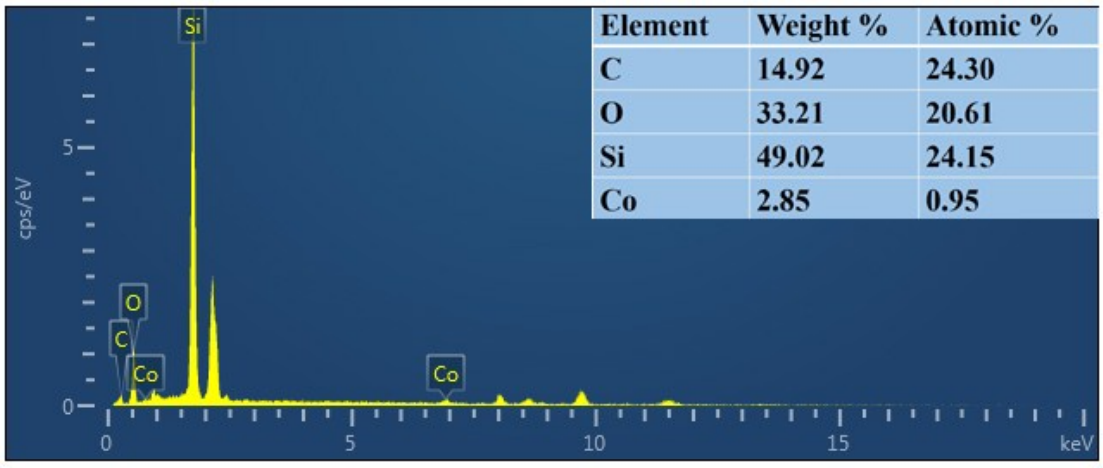


Fig. S1 The cell viability assay of BPA for HepG2 cells.



Element	Weight %	Atomic %
C	14.92	24.30
O	33.21	20.61
Si	49.02	24.15
Co	2.85	0.95

Fig. S2 The energy-dispersive X-ray spectroscopy of SiO_2@Co.

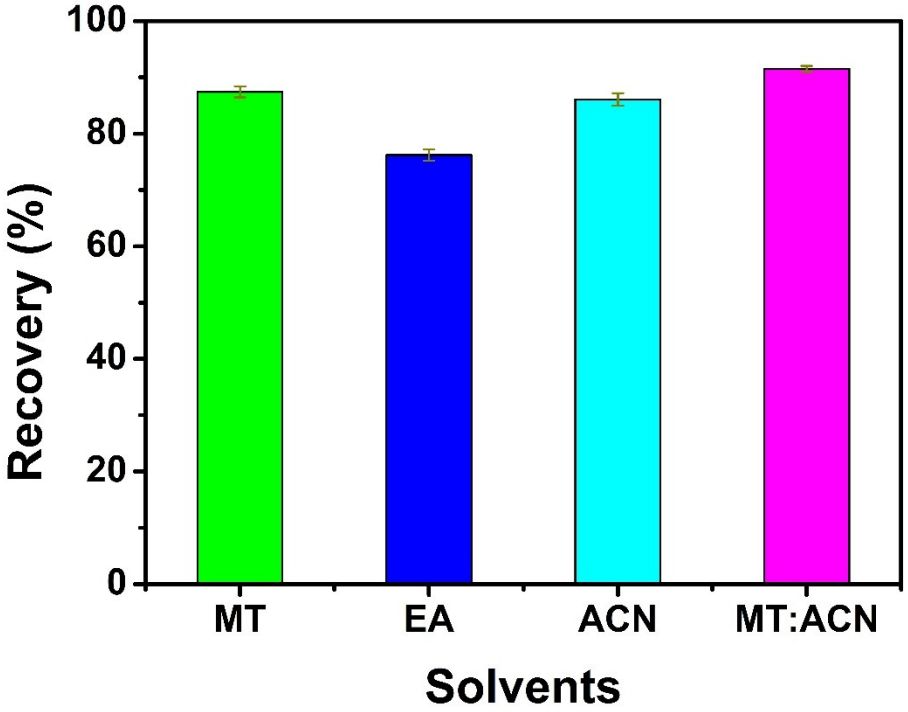


Fig. S3 The optimization of eluents on extraction efficiency.

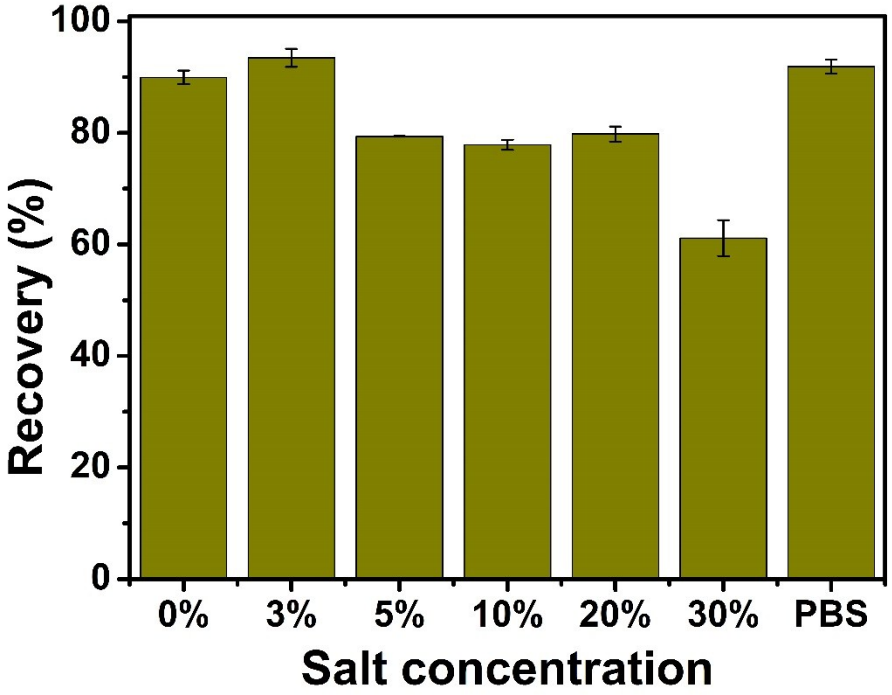


Fig. S4 Effect of concentration of salt on extraction efficiency of C-Co@PST.

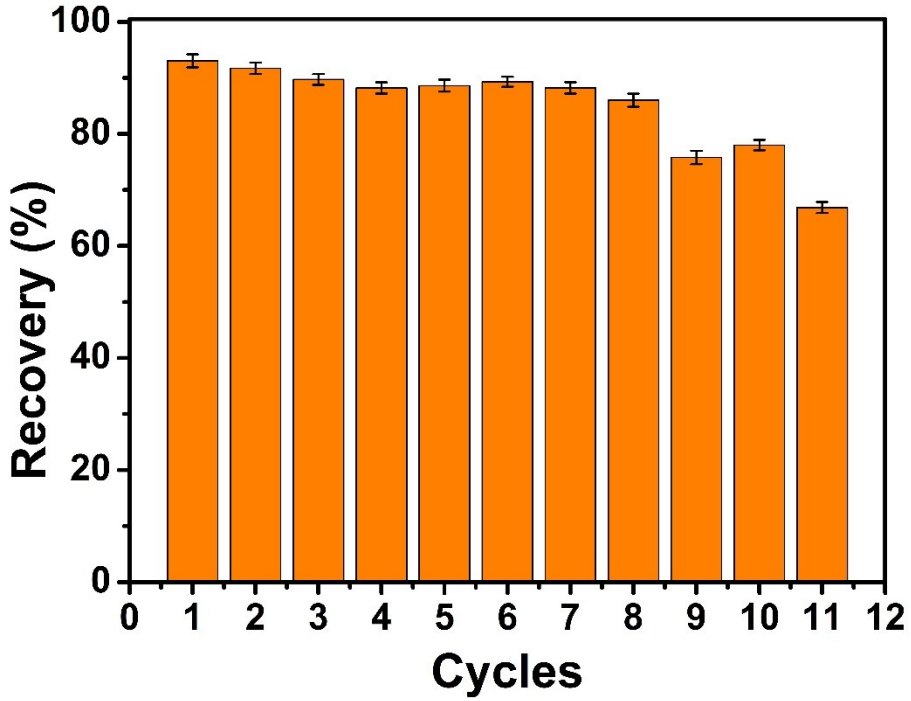


Fig. S5 The reusability of C-Co@PST sorbent for BPA extraction.

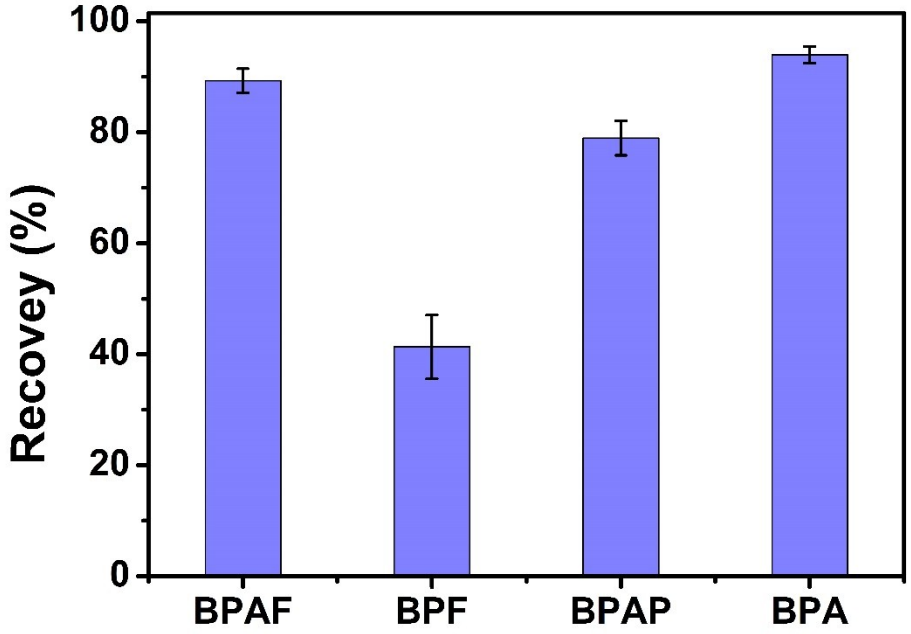


Fig. S6 The extraction recovery of BPAF, BPF, BPAP and BPA on C-Co@PST adsorbent.

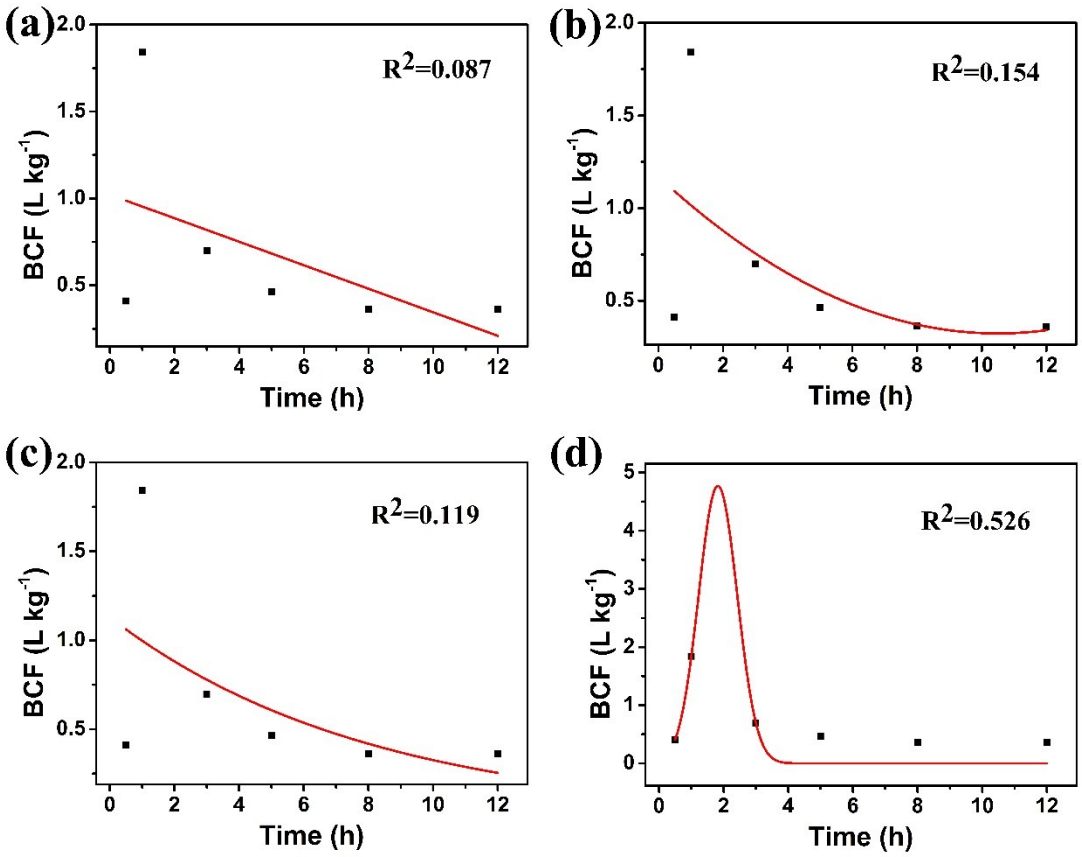


Fig. S7 Different time-dependent BPA prediction models fitting the experimental data from a laboratory-based HpG2 cells–water system: linear model (a), polynomial–linear model (b), exponential model (c), and polynomial–exponential model (d).

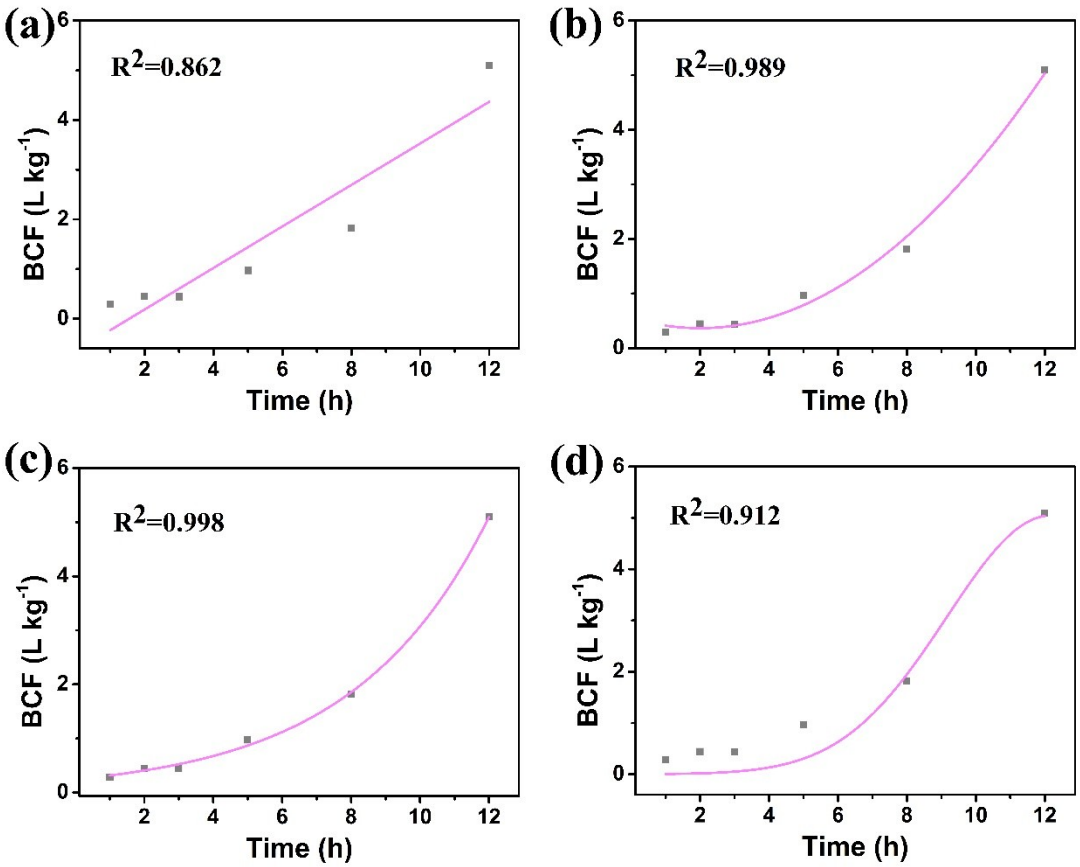


Fig. S8 Different time-dependent BPA prediction models fitting the experimental data from a laboratory-based zebrafishes–water system: linear model (a), polynomial–linear model (b), exponential model (c), and polynomial–exponential model (d).

Table S1 Performance parameters of C-Co@PST based on MSPE.

Matrix	LOD (μg L^{-1})	LOQ (μg L^{-1})	Linear range (μg L^{-1})	r^2	RSD (%, n=5)	
					Inter-day	Intra-day
PBS	0.033	0.10	0.10−200	0.9998	0.21−0.46	0.25−1.60
HepG2 cell	0.050	0.18	0.20−200	0.9963	3.80−3.45	2.52−5.80
Zebrafish	0.110	0.23	0.30−200	0.9946	2.43−5.67	2.10−7.50

Table S2 Recovery of C-Co@PST based MSPE method by spiking experiments in real samples.

Real Samples	Spiking (μg L^{-1}) (n=5, %)	Recovery (%)	Error bar (%)
HepG2 cells	3	88.61	5.79
	30	90.01	3.88
	100	88.90	4.11

Zebrafish samples	3	89.40	7.46
	30	95.60	6.86
	100	88.07	2.06

Table S3 Different time-dependent BPA prediction models and the correlation coefficient (R^2)

Models	Formula	R^2 for HepG2 cell	R^2 for zebrafish
Linear model	$EF(t) = EF_0 + K_u t$	0.0868	0.862
Polynomial linear model	$EF(t) = EF_0 + K_u t + K_e t^2$	0.154	0.989
Exponential model	$EF(t) = EF_0 \times e^{K_u t}$	0.119	0.998
Polynomial exponential model	$EF(t) = EF_0 \times e^{K_u t + K_e t^2}$	0.526	0.915

Table S4 Comparison of some MSPE methods used for determination of BPA.

Real samples	Analytical method	Material	Reusability (Times)	LOD (μg L^{-1})	Sample amount	Linear range (μg L^{-1})	Ref
Milk	MSPE-HPLC-UV	Bmi	---	0.75	1 mL	2.5−5000	S2
---	MSPE-HPLC-FLD	Fe_3O_4@SiO_2@PNIPAM	8	0.58	100 mL	2−200	S3
Human serum	MSPE-HPLC-MS	Fe_3O_4@COF	12	0.0383	10 mL	0.2−50	S4
Water, orange juice and beverage bottle water	MSPE-HPLC-UV	Fe_3O_4@MON-NH_2	4	0.015	20 mL	0.05−200	S5
HepG2 cell and live zebrafish	MSPE-HPLC-FLD	C-Co@PST	8	0.033-0.110	1 mL	0.20−200 for cell; 0.30−200 for fish	This work

Bmi: magnetic active carbon; PNIPAM: N-isopropylacylamide; COF: covalent organic framework; MON-NH_2： amino-functionalized microporous organic network

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