Electronic Supplementary Material (ESI) for Analytical Methods.

A solid phase extraction column based on SiO_2@ZIF-8 for efficient analysis of domoic acid toxins in seawater: Experiment and DFT calculation on adsorption behavior

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1. Experimental section

1.1 Method validation

1. **Selectivity:** By comparing the chromatographic response of blank matrix and series of samples spiked with limit of quantitation (LOQ), low quality control (LQC) and medium quality control (MQC) of ZEN.
2. **Linearity and LOQ:** To establish linearity, six concentrations within a certain range were used to investigate the linear regression equation. The LOQ was determined to be acceptable after five replicates of the lowest calibration standard with the accuracy and precision deviations of <20%.
3. **Precision and accuracy:** The intra- and inter-assay accuracy and precision were evaluated with five replicates at three QC levels to assess the precision and accuracy. Accuracy was indicated by using the percent relative error (RE, %) and the precision was calculated by the percent coefficient of variation (CV, %).
4. **System suitability test (SST):** With guidelines for United States Pharmacopeia (USP), the system suitability test (SST) was implemented to evaluate the performance of the analysis system. According to the reference [*Natural product communications.* 7 (2012) 991-994.], a series of parameters such as theoretical plates (N), tailing factor (T), sensitivity and precision were examined. The calculation formula for these parameters were shown in Table S2.

1.2 System suitability test (SST)

According to the reference (*Natural product communications, 7 (2012) 991-994*), we will examine the system suitability from several parameters such as:

1. **Theoretical plates (N):**

$$N = 5.54\left[\frac{(t_R)}{W_{\frac{1}{2}}}\right]^2$$

t_R was retention time and $W_{\frac{1}{2}}$ is the peak width at half heigh. Theoretical plates should not fall below 2000.

2. **Resolution (R_S) :**

$$R_S = \frac{tR_B - tR_A}{0.5(W_A + W_B)}$$

Where tR_B and tR_A are retention times of peaks A and B, Peak widths W_A and W_B are obtained from the intersection of tangents with baseline. Resolution is considered complete if it

equals or exceeds 1.5

3. Tailing factor (T) :

$$T = \frac{a+b}{2a}$$

a and b are the widths at 5% of peak height. T should be less than or equal to 2 to satisfy the system suitability requirement.

4. Sensitivity

Sensitivity of the method was tested by examining the LOD and LOQ. LOD is used for qualitative analysis, the signal of the sample is 3 times the noise in the blank sample (ratio of signal to noise (S/N)=3); LOQ is used for quantitative analysis (S/N=3).

1.3 interference experiments

The effect of different salt ions was investigated by the addition of various cations (Na^+ and Mg^{2+}) and anions (Cl^- and SO_4^{2-}) at different concentrations (10-200 mmol/L), while other conditions were kept optimal. Relative tolerances for DA recoveries were set to less than 10%.

2. Date

Table S1 Chromatographic conditions

Project	condition
Chromatographic column	Thermo Fisher Hypersil GOLD aQ
Column temperature	25 ℃
Flow rate	200 μL/min
Injection volume	10 μL
Elution procedure	Equal elution
The mobile phase A	0.1 % FA aqueous solution
The mobile phase B	0.1 % FA acetonitrile solution
Mobile phase A : mobile phase B	80%: 20%

Table S2 Mass spectrometry conditions

Project	condition
Ion source	ESI positive ion mode
Spray voltage	3000 V
Capillary temperature	350 ℃
Vaporization temperature	300 ℃
Auxiliary gas	10 bar
Sheath gas	35 bar
Scanning mode	SRM
Collision energy	16 eV
Tube lens	96 V
Analysis of ion transitions	m/z 312→248 for qualitation m/z 312→266 for quantification

Table S3 Calibration equation, limitation of detection (LOD) and limit of quantitation (LOQ) *

Linear range (ng/L)	Calibration equation	Correlation coefficient (R)	LOD (ng/L))	LOQ (ng/L))
12.0~5000.0	y=1197.51(± 22.99)x+212.95(± 25.52)	0.9999	4.0	12.0

Table S4 System suitability parameters for Apt@PSM monolithic column coupled to HPLC

Compounds	Retention time (min)	Theoretical plates	Tailing factor	Sensitivity (ng/L)	Precision* (%, n = 6)
DA	2.72	11038	0.99	4.0	3.8

*: Precision was calculated through the relative standard deviation (RSD) of six replicate injections.

Table S5 The interference of ionic species on the determination of DA.

Ionic species	Tolerance level (mmol/L)
Cl^-、Na^+、	200
Mg^{2+}	120
SO_4^{2-}	80

Table S6 Comparison of SiO_2@ZIF-8 with other reported adsorbents.

Adsorbents	Pretreatment method	LODs (ng/L)	Linear range (ng/L)	Recovery (%)	Ref.
Octadecyl	SPE	5.0	25.0-7500.0	94±2%-99±2%	[30]
magnetic molecularly imprinting polymers	MSPE	50000.0	100000.0-6000000.0	90.5%-92.1%	[31]
magnetic molecularly imprinted silica	MSPE	200000.0	100000.0-6200000.0	87.6±7.0%-88.3±6.2%	[33]
SiO_2@ZIF-8	SPE	4.0	12.0-5000.0	86.1±3.2%-93.6±1.1%	This work

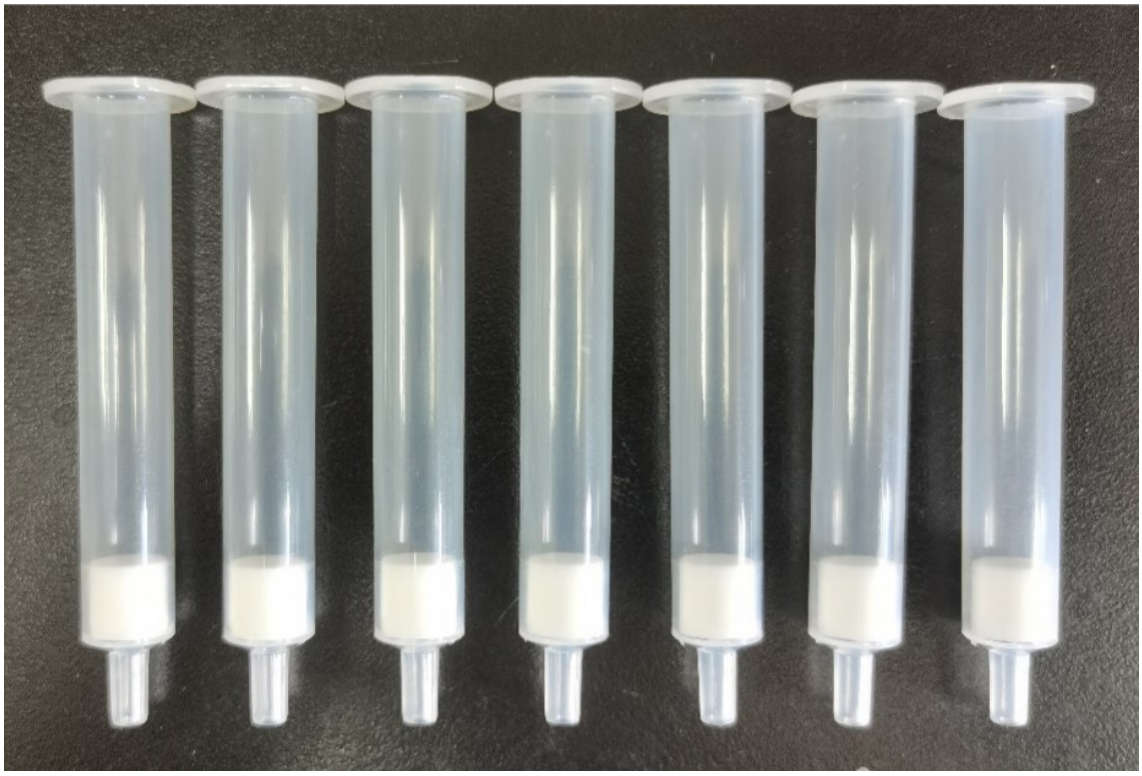

Figure S1 The physical map of SiO_2@ZIF-8 column

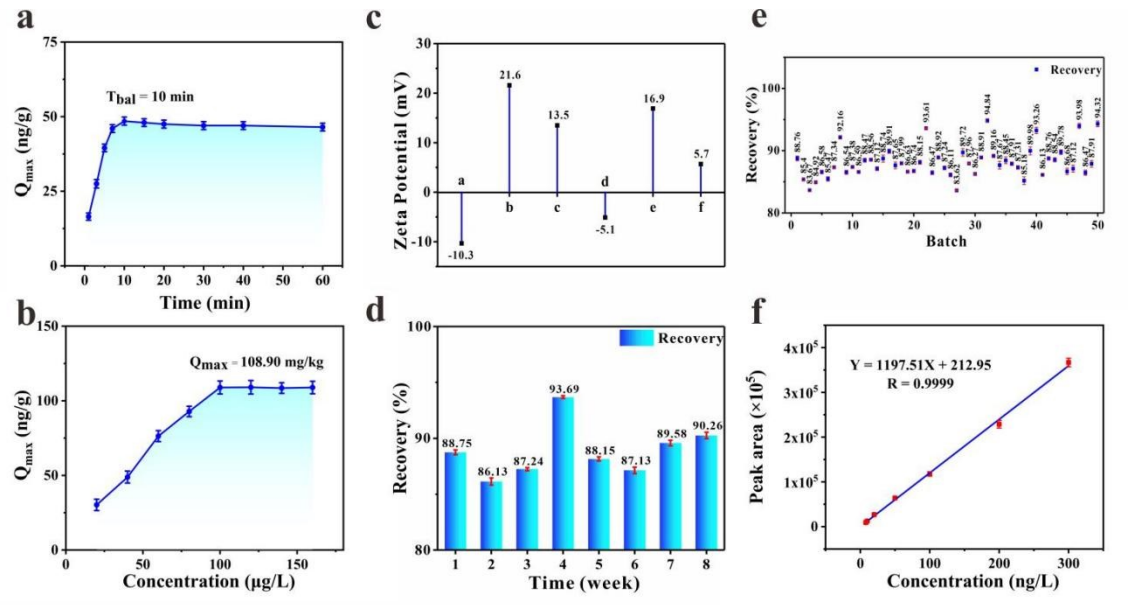

Figure S2 (a) The adsorption dynamics curve of DA by SiO_2@ZIF-8, (b) The adsorption isotherm, (c) Zeta potential of a: DA, b: ZIF-8, c: ZIF-8 after adsorbing DA, d: SiO_2, e: SiO_2@ZIF-8 and f: SiO_2@ZIF-8 after adsorbing DA, (d) Recovery rates of SiO_2@ZIF-8 columns from same batches, (e) Recovery rates of SiO_2@ZIF-8 columns from different batches, (f) Standard work curve of DA in seawater.