Supplementary Information

$Cr_2TiC_2T_x$ MXene as an adsorbent material in ultrasonic-assisted d-μ-solid phase extraction for trace detection of heavy metals

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The sample preparation, d-μ-SPE process, and analytical calculations were performed as reported in our previous work.[1]

ESI-1 Sample preparation and digestion process.

All food samples were processed according to our previous report.[1] In brief, food samples were purchased from local markets in Lincoln, Nebraska, USA and were washed and dried in air. The agricultural products were dehydrated at 80 °C for 24 h before grinding. A soil sample was collected from a local farm in Lincoln, Nebraska, USA. Next, powdered food samples were digested in concentrated nitric acid in polyethylene (PE) containers at 100 °C for 4 h. If necessary (when HNO_3 evaporated to less than 2 mL), more HNO_3 was added to the containers. To each of the resulting digestion solutions, 1-5 mL of hydrogen peroxide (30%) was added dropwise at elevated temperature (120 °C) until the liquids became colorless and transparent. For the soil sample, 100 mg of soil was etched in 20 mL of concentrated HCl at 50 °C for 5 h. After cooling down, the solution was centrifuged to produce a clear liquid. Finally, the digestion solution was filtered and diluted for further experiments.

ESI-2 d-μ-SPE process and real-life sample analysis

Briefly, for the adsorption step in the d-μ-SPE process, 10 mL samples containing 2 mg L^{-1} of Cd^{2+} and Pb^{2+} were mixed with $Cr_2TiC_2T_x$ MXene and sonicated. At this step, the pH, mass of adsorbent, and sonication time were optimized (see Figure 3b-d). After completing the adsorption step, samples were centrifuged, supernatant solutions were filtered using 0.45 μm Whatman syringe filters, and the concentrations of the

supernatant solutions were measured.

After performing the adsorption under optimized conditions, the $Cr_2TiC_2T_x$ MXene adsorbent was collected and used for desorption studies. Here, the $Cr_2TiC_2T_x$ MXene containing heavy metals was subjected to a desorption process using inorganic acids and sonicated as part of the preliminary test to find the suitable desorption eluent. Similar to the adsorption step, we used *one-variable-at-a-time method* to optimize the parameters of the desorption step; see Figure 3e-g. Finally, the acid solutions were analyzed by FAAS, and relative recoveries were calculated.

After digesting the real-life samples and diluting the solutions, heavy metal ions in these samples were preconcentrated using the $Cr_2TiC_2T_x$ MXene-based d-μ-SPE process under the optimized conditions (as summarized in Table 1) and analyzed by FAAS.

ESI-3 Analytical performance calculations

Analytical calibration curves were plotted to assess the performance of the proposed method, as well as to calculate the limit of quantification (LOQ), the limit of detection (LOD), and the linear dynamic range (LDR).[1, 2]

LOQ, defined as the lowest concentration or signal (multiple measurements) for an analytical method within an accuracy of 85%-115% and a precision of ≤ 10%,[3] was calculated as $LOQ= 10S_b/m$, where S_b is the standard deviation of six consecutive measurements of a blank sample and m is the slope of the analytical calibration curve.

LOD, defined as the lowest signal from an analyte that can be detected with at least 95% probability,[3] was calculated as $LOD= 3.3\ S_b/m$, where S_b is the standard

deviation of six consecutive measurements of a blank sample and m is the slope of the analytical calibration curve.

In this study, concentrations are reported as (Mean ± tS) / $N^{1/2}$ to show the accuracy of the recorded signals. **Mean** is the average of the recorded concentrations, **t** is the t value from the t-test table, **S** is the standard deviation, and **N** is the number of signal readings (typically N=3). Also, extraction recovery is calculated as described in **Eqn. 1**:

$$ER = \frac{C_F}{C_0} \times 100\% \quad \textbf{Eqn. 1}$$

where C_F is the final recovered concentration after desorption, and C is the initial concentration.

The total concentration (C_T) of heavy metals in a spiked sample was determined using **Eqn. 2**, where C_0 is the initial concentration of heavy metals and C_S is the concentration for spiked heavy metals:

$$C_T = (C_0 + C_s) \pm SD \quad \textbf{Eqn. 2}$$

Relative recovery is a measure of accuracy when reporting the heavy metal contents in real-life samples and is calculated using **Eqn. 3**:

$$RR = \frac{C_T - C_0}{C_s} \times 100\% \quad \textbf{Eqn. 3}$$

Any significant deviation is a sign of error in the process.

Standard deviation (**Eqn. 4**) is a measure of the precision or closeness of the collected data. SD (σ) is defined as follows:

$$\sigma = \left(\frac{\sum(x_i-\mu)^2}{N-1}\right)^{\frac{1}{2}}$$ **Eqn. 4**

where X_i is the recorded signal for each reading, μ is the mean value, and N is the number of readings for each experiment (typically N>3).

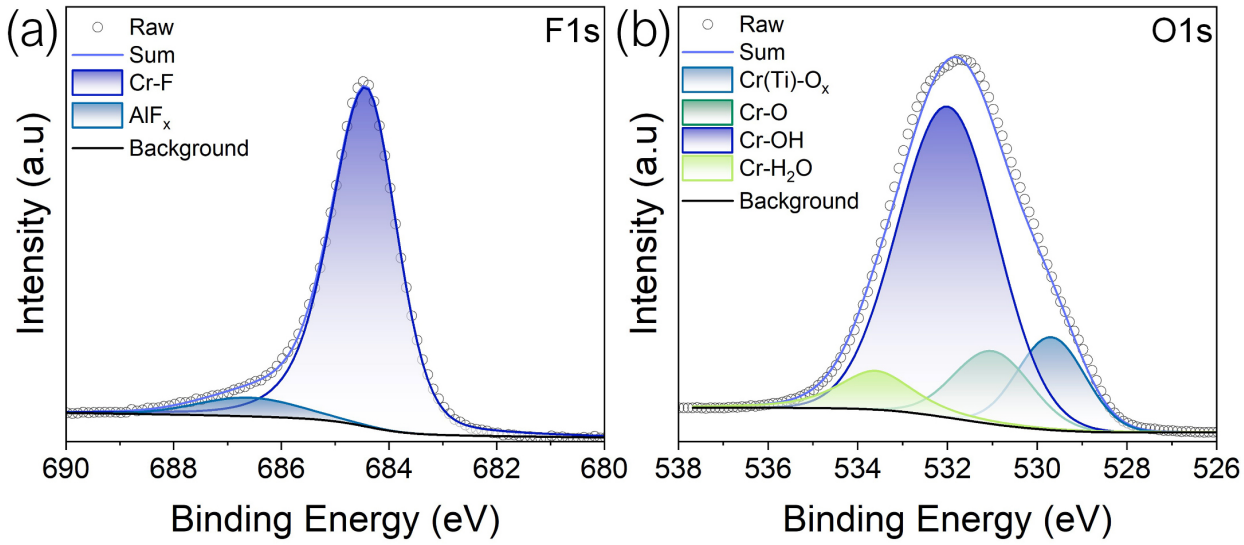

Fig. S1. High-resolution XPS spectra of (a) F1*s* and (b) O1*s* regions for $Cr_2TiC_2T_x$ MXene.

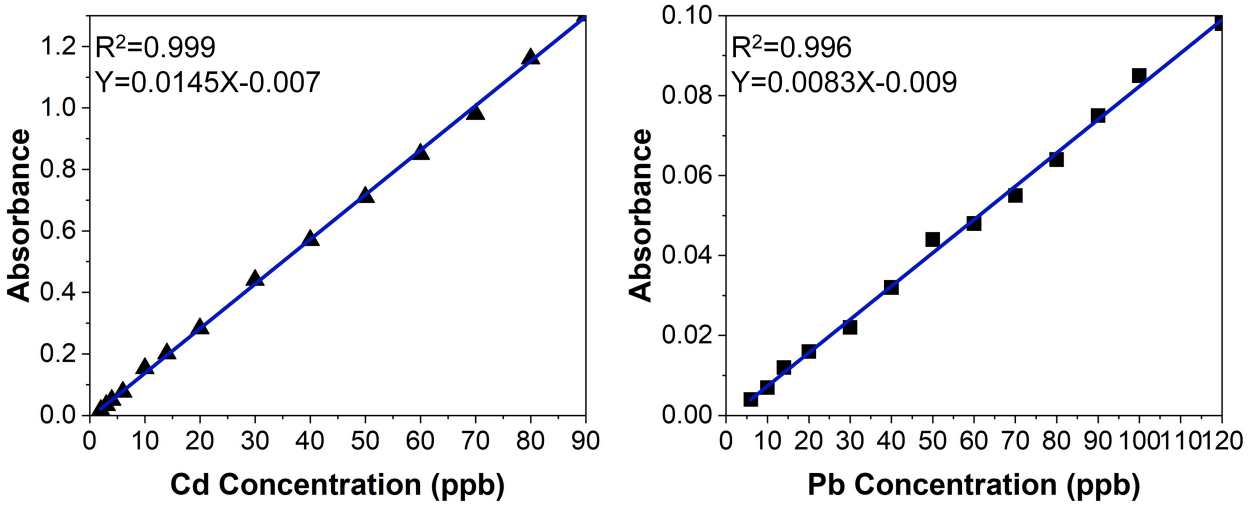

Fig. S2 Analytical calibration curves for cadmium and lead ions.

Table S1 Effect of interfering ions on the determination of cadmium and lead ions.

Interfering ion	Tolerable concentration ratio X/Cd and Pb	*RR*[a]% ± *SD*[b]	
		Pb	Cd
Na^+	2,500	102.34±1.28	101.18±1.71
K^+	2,500	100.25±1.15	99.78±2.75
Mg^{2+}	400	99.85±1.73	100.13±1.25
Ca^{2+}	400	100.72±1.73	100.73±1.86
Zn^{2+}	250	99.67±1.82	100.18±1.82

[a] Relative Recovery [b] Standard Deviation

Table S2 Determination of cadmium and lead ions in certified reference materials

Sample	Element	Certified concentration (mg Kg^{-1})	Found (mg Kg^{-1})	Relative error (%)
Taiwan Clay Soil (CRM046)	Cd[a]	7.01 ± 0.177	6.98±0.22	-0.42
	Pb[b]	45.3 ± 1.92	44.87±0.78	-0.95

[a] Traceable to NIST SRM 3108 Lot 060531 [b] Traceable to NIST SRM 3128 Lot 030721

ESI-4 Raw data collected for Figure 3

The following tables summarize the raw data we collected for the optimization of $Cr_2TiC_2T_x$-d-µ-SPE.

Table S3. Raw data for adsorption step.

Adsorption														
pH					Adsorbent Mass					Sonication Time				
	cadmium		Lead			cadmium		Lead			cadmium		Lead	
Value	Removal (%)	St. Dev. (%)	Removal (%)	St. Dev. (%)	Value (mg)	Removal (%)	St. Dev. (%)	Removal (%)	St. Dev. (%)	Value (s)	Removal (%)	St. Dev. (%)	Removal (%)	St. Dev. (%)
4	61	3	69	1.5	1	72	1.5	87	2.7	60	64	1.5	59	1.5
5	77	1.8	81	2	3	95	1.9	99	1.5	90	75	2	72	1.9
6	99	1.5	99	1.8	5	99	2.2	99	2.9	120	81	3.1	81	3.1
7	99	2	93	2.1	10	99	1.5	99	1.9	150	99	2.1	99	1.7
8	95	1.3	83	2.5	15	99	1.1	99	1.4	180	99	1.6	99	2.1
9	92	1.1	80	1.1						240	99	3.1	91	1.1
										300	91	2	88	1.1

Table S4. Raw data for desorption step.

Desorption														
Eluent					Volume					Sonication Time				
	Cadmium		Lead			Cadmium		Lead			Cadmium		Lead	
Type	RR (%)	St. Dev. (%)	RR (%)	St. Dev. (%)	Value (mL)	RR (%)	St. Dev. (%)	RR (%)	St. Dev. (%)	Value (s)	RR (%)	St. Dev. (%)	RR (%)	St. Dev. (%)
AcOH	58	2.5	54	1	0.5	38	2.1	45	3.3	60	64	3.2	63	1.8
HNO_3	99	1.8	99	1.1	1	70	1	71	1.5	120	75	1.5	46	3
HCl	99	2.1	99	1.2	1.5	95	0.9	93	3.1	180	81	2	80	1.5
					2	99	3	99	2	240	90	1	92	2.5
					2.5	99	2.3	99	1.8	300	99	1.9	99	1.3
					3	99	1	99	2.8	360	99	3.2	99	1.8
										420	99	1.8	99	1

Supplementary references:

1. S. Bagheri, R. Chilcott, S. Luo and A. Sinitskii, *Langmuir*, 2022, **38**, 12924–12934.
2. M. Behbahani, G. Rabiee, S. Bagheri and M. M. Amini, *Microchemical Journal*, 2022, **183**, 107951.
3. M. Behbahani, V. Zarezade, A. Veisi, F. Omidi and S. Bagheri, *International Journal of Environmental Science and Technology*, 2019, **16**, 6431-6440.