

Supporting information

Amorphous Phosphated Titanium Oxide with Amino and Hydroxyl Bifunctional Groups for Highly Efficient Heavy Metals Removal

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Structure characterization

X-ray diffraction (XRD) characterization of the samples was carried out on a German Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu K α radiation at 40 kV and 40 mA. Transmission electron microscopy (TEM) images were achieved on a JEOL-2100F TEM operated at an acceleration voltage of 200 kV. A JEM 2100F electron microscope operating at 200 kV equipped with an EDX unit (Si (Li) detector) was used for the HR-TEM investigations. Nitrogen adsorption/desorption isotherms were measured at -196°C on a Micromeritics ASAP 2460 analyzer. Samples were degassed at 200°C for 24 h prior to the measurement. Scanning electron microscopy (SEM) images were obtained by Hitachi-S4800. The functional amorphous titanium oxide materials before and after heavy metal ions adsorption were pressed into tablets with KBr powder and then detected by Fourier transform infrared spectrometer (FT-IR, Perkin Elmer, USA) with the scanning range from 400 to 4000 cm⁻¹. TG measurements were conducted on a Netzsch STA 449C TG–DSC thermoanalyzer. The flow rate of the carrier gas (air) was 30 mL min⁻¹. The temperature was raised from room temperature to 700 °C with a ramp rate of 10 °C min⁻¹. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method with the adsorption data at the relative pressure (P/P₀) range of 0.05-0.2. The total pore volumes were estimated at P/P₀ = 0.99. The average pore diameter was analyzed with Barrett-Joyner-Halenda (BJE) method. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with Thermo Scientific, ESCALAB 250Xi. The measuring spot size was 500 μ m and the binding energies were calibrated by referencing the C 1s peak (284.8 eV). The zeta potentials at various solution pH ranging from 1 to 10 were measured using Zeta sizer Nano-Z (Malvern, UK).

Adsorption experiments.

Aqueous solutions containing different concentrations of heavy metal ions (0.02 - 0.5 mmol/L) have been prepared. In this case, Cd(NO₃)₂·4H₂O, Cr(NO₃)₃·9H₂O, Pb(NO₃)₂·3H₂O and Fe(NO₃)₃ were used as the source of Cd²⁺, Cr³⁺, Pb²⁺ and Fe³⁺ respectively. The pH of solution was adjusted by adding NaOH (0.1 M) and HNO₃ (0.1 M) solutions. All adsorption experiments were carried out at room temperature (25°C). The general experimental process is described as follows: 20 mg of adsorbent was added to 200 mL of Cd²⁺, Cr³⁺, Pb²⁺ and Fe³⁺ solution under stirring for 480 min. In this case, the pH of heavy metal ions solution was adjusted to 4.0. After a specified time, the solid and liquid were separated immediately by centrifugation with a speed of 12,000 rpm for 5 min. The concentration of heavy metal ions in the liquid analyzed by inductively coupled plasma mass

spectrometer (Thermo scientific ICAP, RQ, USA). The effect of pH on adsorption of heavy metal ions were studied by varying the pH of heavy metal ions solution from 2.0 to 7.0. In pH effect studies, the weight of adsorbent, the volume and initial concentration of heavy metal ions solutions are the same as these used in the adsorption rate tests. In this case, the contact time of adsorbent with solutions was set at 480 min.

The adsorption capacity (q_e) for heavy metal ions was calculated according to the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

$$R_e = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

$$K_d = \frac{(C_0 - C_e)V}{C_e m} \quad (3)$$

where C_0 and C_e represent the initial and equilibrium heavy metal ions concentrations (ug mL^{-1}), respectively, K_d is the distribution coefficient, V is the volume of the metal ion solutions (mL), and m is the amount of adsorbent (mg). R_e (%) is the removal efficiency.

Adsorption Kinetics

The rate of adsorption was determined by using two different rate equations. Pseudo-first-order and pseudo-second-order mechanisms were investigated for determining adsorption behaviors.

The equation for pseudo-first order kinetics is presented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

The equation for pseudo-second order kinetics is presented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_t and q_e are the adsorption capacities of heavy metals at time t and at equilibrium time (mg/g). k_1 is the rate constant of the pseudo-first order adsorption process (min^{-1}). The values of k_1 and q_e can be calculated from the slope and intercept of plots of $\log(q_e - q_t)$ versus t . Where k_2 is the rate constant of the pseudo-second order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), which can be obtained by a plot of t/q_t against t .

The Elovich equation established through the work of Zeldowitsch is presented as follows:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln[\ln(t)] \quad (6)$$

where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is desorption rate constant (g mg^{-1}) during any experiment. A plot of Q_t versus $\ln(t)$ should yield a linear relationship with a slope of $1/\beta$ and an intercept of $(1/\beta) \ln(\alpha\beta)$.

Adsorption isotherm measurement.

For adsorption isotherm studies, 20 mg of adsorbent was added into 200 mL of heavy metal ions solution with various concentrations (0.05 - 0.5 mmol/L). The pH of heavy metal ions solution was adjusted to 4.0. The mixture was kept at room temperature under stirring for 480 min. Subsequently, the concentration of heavy metal ions was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5110, USA). Langmuir and Freundlich adsorption models are employed to analyze experimental data.

The equation for the Langmuir isotherm is presented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{cal}K_L} + \frac{C_e}{q_{cal}} \quad (7)$$

The equation for the the Freundlich isotherm is described as:

$$\log(q_e) = \frac{1}{n} \log(C_e) + \log K_F \quad (8)$$

where q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), q_{cal} represents the maximum adsorption capacity of adsorbents (mg/g), and K_L is the Langmuir adsorption constant (L/mg). K_F ($\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$) represents the sorption capacity when the equilibrium concentration of adsorbate equals to 1, and n represents the degree of sorption dependence with equilibrium concentration. The q_{cal} and b are calculated from the slope and intercept of the linear plot of C_e/q_e against C_e . The values of K_F and n can be obtained from the intercept and the slope of the linear plot of $\log(q_e)$ versus $\log(C_e)$.

Effect of co-existing cations, anion and HA on heavy metal ion sorption

20 mg of adsorbent was added into 200 ml of heavy metal ions solution containing CaCl_2 , NaF and humic acid (HA) with various concentrations (10 - 50 mg/L). The pH of heavy metal ions solution was adjusted to 4.0. The mixture was kept at room temperature under stirring for 480 min.

Subsequently, by using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5110, USA) to determine the residual heavy metal ions content in the remaining solution.

Recycle performance

To study the re-adsorption capacity of functional amorphous phosphated titanium oxide, 20 mg of adsorbent was added to 200 mL of heavy metal ions solution (Cd^{2+} , Cr^{3+} , Fe^{3+} and Pb^{2+} with concentrations of 0.05 mmol/L) under stirring for 480 min. In this case, the pH of solution was adjusted to 4.0. Regeneration of the used adsorbent was carried out using 1.0 M HCl. Later, the adsorbent was washed with distilled water, and dried under vacuum overnight for next adsorption experiments.

The van't Hoff equations as follows:

$$\Delta G = -RT \ln K_L \quad (9)$$

$$\ln K_F = -\frac{\Delta H^0}{RT} + \frac{\Delta S_0}{RT} \quad (10)$$

where R (8.314 J mol⁻¹ K⁻¹) is the gas constant, T (K) is the absolute temperature. ΔG^0 , ΔH^0 and ΔS^0 are the changes in Gibbs free energy, enthalpy and entropy, respectively. ΔH^0 and ΔS^0 were obtained from the slope and the intercept of the plot of $\ln K_F$ vs. $1/T$.

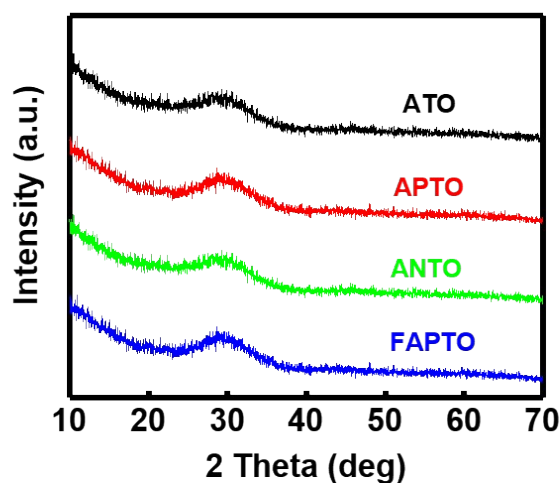


Fig. S1 XRD patterns of all samples.

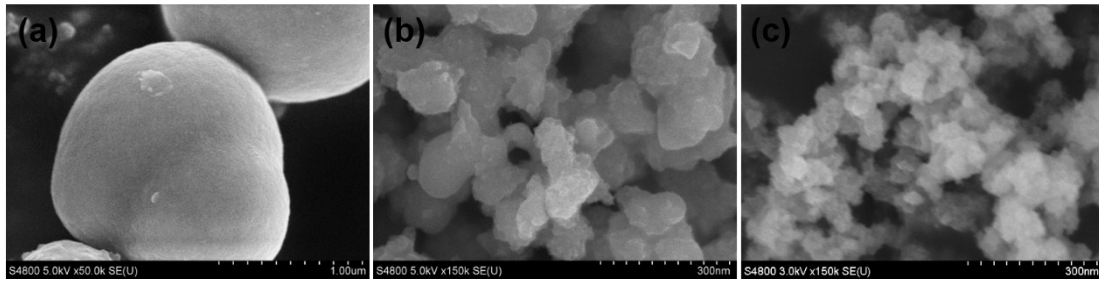


Fig. S2 SEM of (a) ATO, (b) APTO, and (c) ANTO.

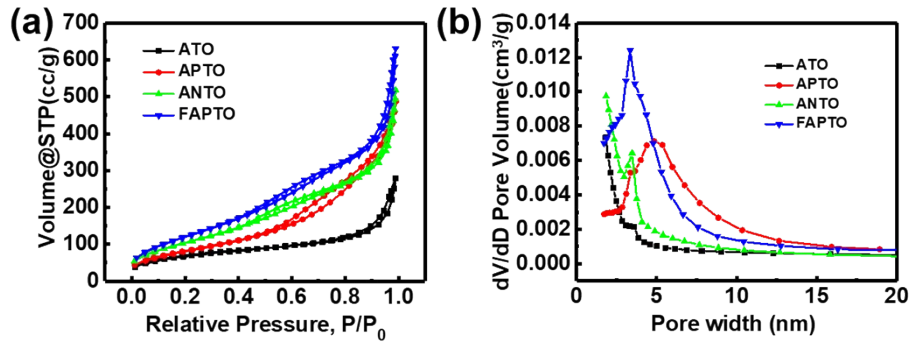


Fig. S3 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of all samples.

Table S1 Textural properties of samples calculated from N₂ adsorption isotherms.

Samples	SSA (m ² /g)	Volume (cm ³ /g)	Average pore size (nm)
ATO	244	0.37	9.7
APTO	395	0.74	7.3
ANTO	373	0.38	5.3
FAPTO	446	1.12	5.6

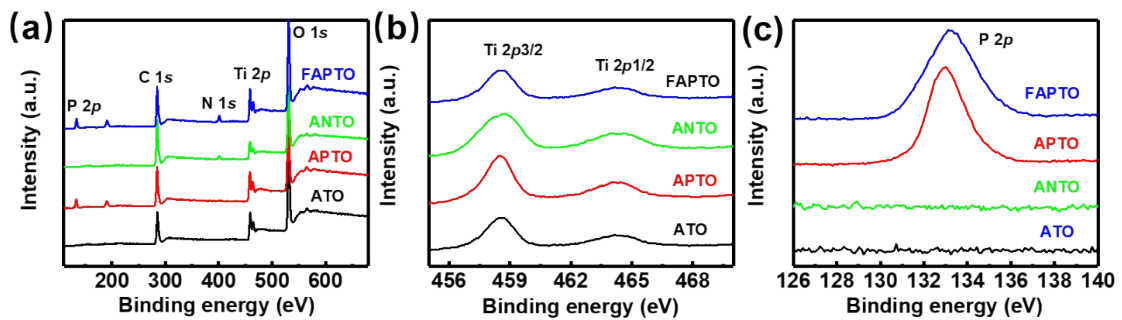


Fig. S4 (a) The full XPS spectrum; (b) High-resolution XPS spectrum of Ti 2*p*; (c) High-resolution XPS spectrum of P 2*p* of ATO, APTO, ANTO and FAPTO.

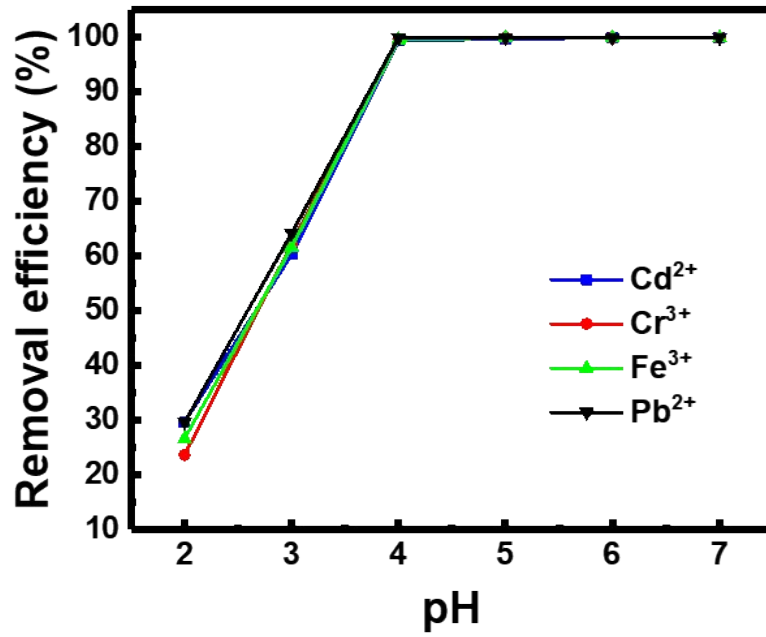


Fig. S5 Effect of solution pH on the adsorption of FAPTO. $C_0 \sim 5$ mg/L; $m = 0.020$ g; $V = 200$ mL; Contact time: $t = 480$ min.

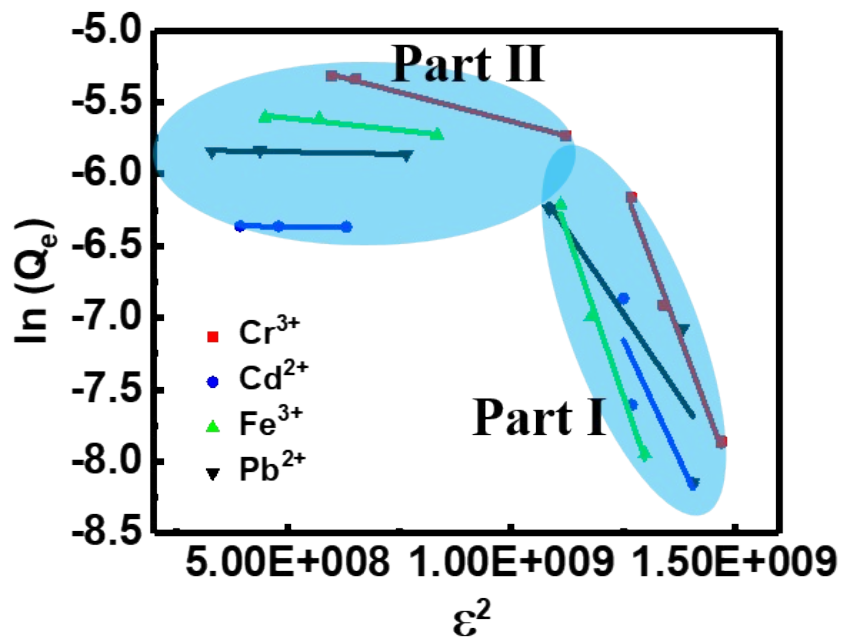


Fig. S6 A plot of $\ln(Q_e)$ versus ϵ^2 .

Table S2 Kinetic parameters and equations (D-R isotherm model) for adsorbing heavy metal ions onto FAPTO.

Single ions		Equations	E (kJ mol ⁻¹)	R ²
Part	Pb ²⁺	$Y = -1.23 - 4.58 \times 10^{-9}x$	10.4	0.8434
	Cr ³⁺	$Y = 4.33 - 6.32 \times 10^{-9}x$	8.9	0.9920
I	Cd ²⁺	$Y = 1.15 - 4.64 \times 10^{-9}x$	10.4	0.7671
	Fe ³⁺	$Y = 3.76 - 7.13 \times 10^{-9}x$	8.4	0.9897
Part	Pb ²⁺	$Y = -5.81 - 3.96 \times 10^{-11}x$	113	0.8155
	Cr ³⁺	$Y = -4.82 - 8.09 \times 10^{-10}x$	24.9	0.9969
I I	Cd ²⁺	$Y = -6.35 - 2.01 \times 10^{-11}x$	158	0.9767
	Fe ³⁺	$Y = -5.44 - 3.37 \times 10^{-10}x$	38.6	0.9315

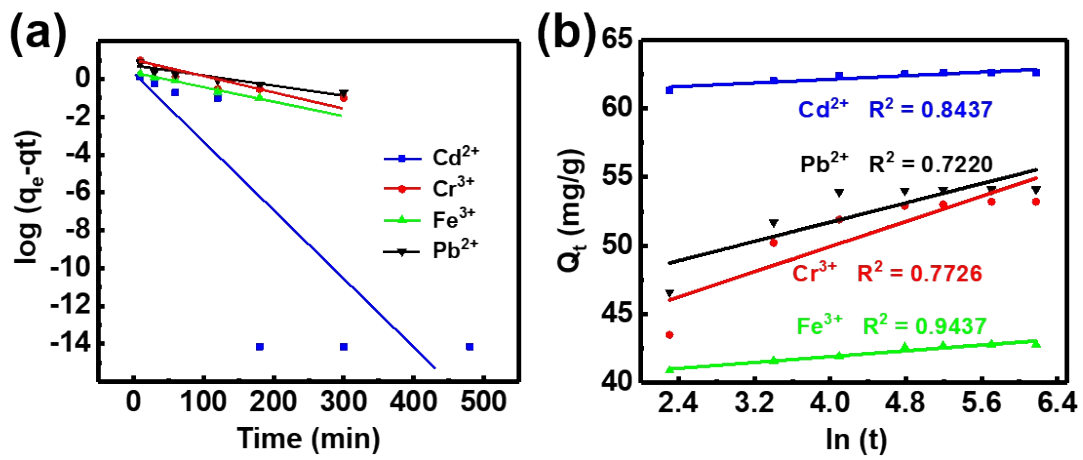


Fig. S7. (a) The pseudo-first order and (b) the Elovich model kinetics plot of FAPTO.

Table S3. Kinetic parameters (Elovich Model) for adsorbing heavy metal ions onto FAPTO.

Single ions	$(1/\beta)\ln(\alpha\beta)$	β (g mg ⁻¹)	R ²
Pb ²⁺	53.99	0.57	0.7220
Cr ³⁺	53.20	1.89	0.7726
Cd ²⁺	62.60	3.37	0.8437

Fe ³⁺	42.80	0.44	0.9437
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Table S4. Kinetic parameters (Pseudo-First-Order Model) for adsorbing heavy metal ions onto FAPTO.

Single ions	q _{e,exp} (mg/g)	k ₁	q _{e,cal} (mg/g)	R ²
Pb ²⁺	53.99	0.0143	4.35	0.8469
Cr ³⁺	53.20	0.0111	4.44	0.9194
Cd ²⁺	62.60	0.0838	1.54	0.7100
Fe ³⁺	42.80	0.0179	2.20	0.7814

Table S5. Kinetic parameters (Pseudo-Second-Order Model) for adsorbing heavy metal ions onto FAPTO.

Single ions	q _{e,exp} (mg/g)	k ₂	q _{e,cal} (mg/g)	R ²
Pb ²⁺	53.99	0.0085	54.01	0.9998
Cr ³⁺	53.20	0.0103	53.42	0.9999
Cd ²⁺	62.60	0.0699	62.66	0.9999
Fe ³⁺	42.80	0.0267	42.88	0.9999

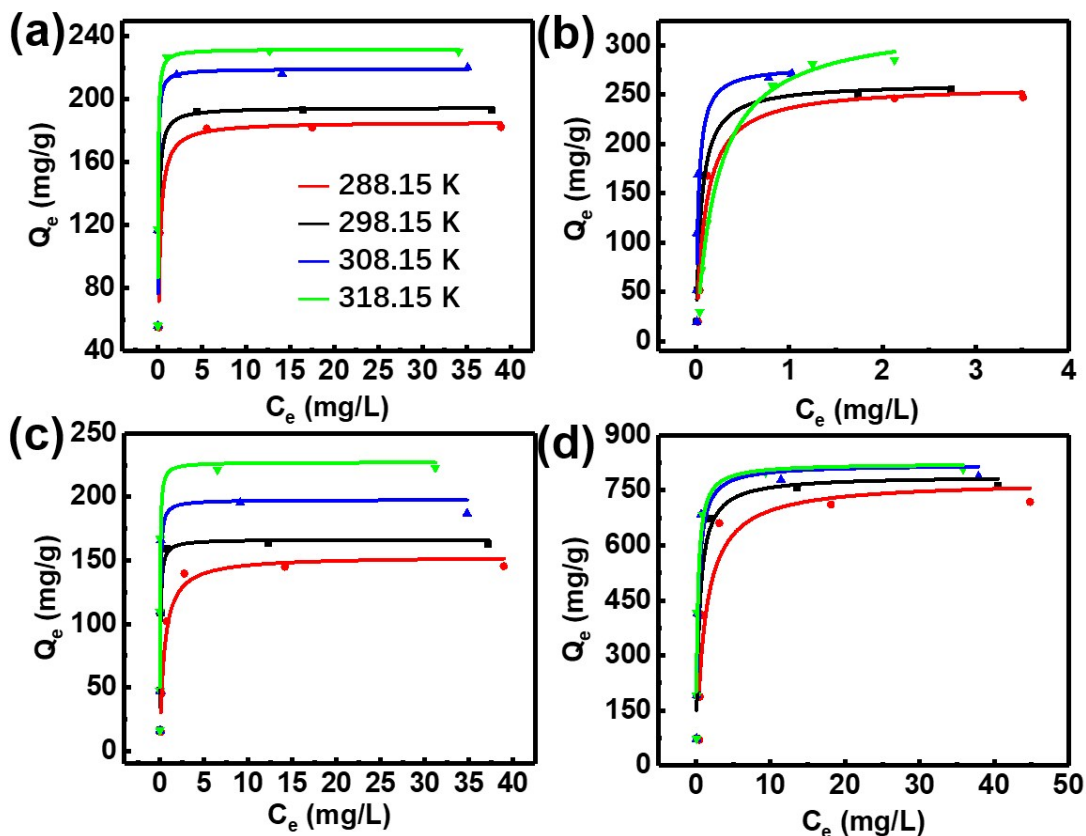


Fig. S8. The Langmuir equilibrium isotherm of (a) Cd^{2+} ; (b) Cr^{3+} ; (c) Fe^{3+} and (d) Pb^{2+} onto FAPTO at different temperature. ($C_0(\text{Cd}^{2+}) = 6.3 - 57.1 \text{ mg/L}$; $C_0(\text{Cr}^{3+}) = 5.3 - 28.2 \text{ mg/L}$; $C_0(\text{Fe}^{3+}) = 4.3 - 54.4 \text{ mg/L}$; $C_0(\text{Pb}^{2+}) = 5.4 - 116.3 \text{ mg/L}$; $m = 0.020 \text{ g}$; $V = 200 \text{ mL}$; $t = 480 \text{ min}$; $T = 298.15 \text{ K}$; $m = 0.020 \text{ g}$; $V = 200 \text{ mL}$; Contact time: $t = 480 \text{ min}$.)

Table S6. Parameters of the Langmuir and Freundlich Isotherm for Heavy Metal Ions Adsorption onto FAPTO at different temperature.

T (K)	Single ions	Langmuir model			Freundlich model		
		q_{cal} (mg/g)	K_L (L/mg)	R^2	K_F ($\text{mg}^{1-n}\text{L}^n/\text{g}$)	n	R^2
288.15	Pb^{2+}	775.2	1.86	0.9039	337.81	4	0.6982
	Cr^{3+}	259.4	10.20	0.9593	191.74	3	0.8394
	Cd^{2+}	185.7	5.25	0.9588	120.40	7	0.7964
	Fe^{3+}	153.1	8.07	0.9734	83.18	5	0.7204
298.15	Pb^{2+}	788.4	2.14	0.9687	415.59	5	0.7456
	Cr^{3+}	261.7	19.35	0.9802	211.79	4	0.8523

	Cd ²⁺	194.5	11.86	0.9879	133.74	8	0.7913
	Fe ³⁺	166.4	17.46	0.9798	113.75	8	0.7456
308.15	Pb ²⁺	819.9	3.69	0.9219	458.23	6	0.6883
	Cr ³⁺	279.3	39.90	0.9724	278.22	4	0.8142
	Cd ²⁺	219.4	26.66	0.9642	157.22	8	0.8082
	Fe ³⁺	197.6	26.87	0.8694	132.05	8	0.6163
318.15	Pb ²⁺	823.3	4.66	0.9343	477.40	6	0.7349
	Cr ³⁺	324.2	45.01	0.9917	239.80	3	0.9260
	Cd ²⁺	232.0	29.92	0.9286	169.44	8	0.7495
	Fe ³⁺	227.2	35.65	0.8888	150.74	7	0.6958

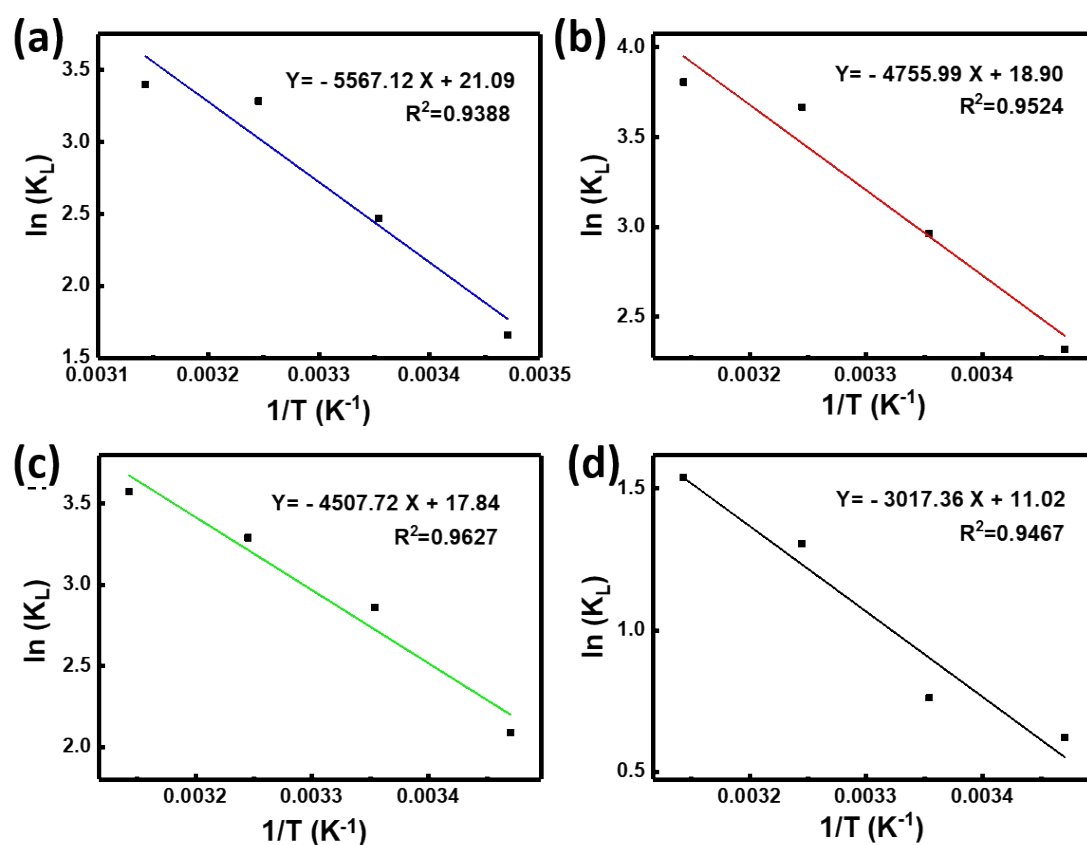


Fig. S9 Van't Hoff plots for the adsorption of (a) Cd²⁺; (b) Cr³⁺; (c) Fe³⁺ and (d) Pb²⁺ onto FAPTO.

Table S7. Thermodynamic Parameters of heavy metal ions Adsorption on FAPTO.

T (K)	Single ions	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
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288.15	Cd ²⁺	-3.97	46.28	175.34
289.15		-6.13		
308.15		-8.41		
318.15		-8.99		
288.15	Cr ³⁺	-5.56	39.54	157.13
289.15		-7.34		
308.15		-9.40		
318.15		-10.07		
288.15	Fe ³⁺	-5.00	37.48	148.32
289.15		-7.09		
308.15		-8.43		
318.15		-9.45		
288.15	Pb ²⁺	-1.49	25.09	91.62
289.15		-1.89		
308.15		-3.34		
318.15		-4.07		

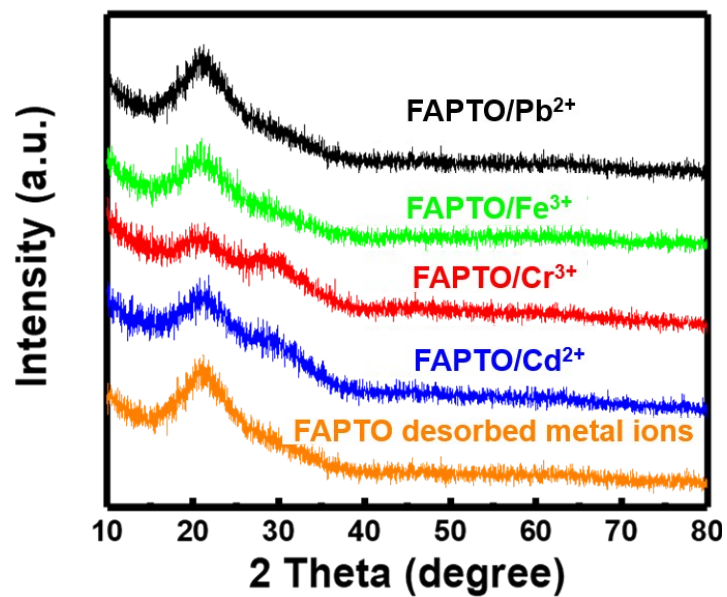


Fig. S10 The XRD patterns of FAPTO-10 after Cd^{2+} , Cr^{3+} , Fe^{3+} and Pb^{2+} adsorption.