K-Co-Mo-S_x Chalcogel: High-Capacity Removal of Pb^{2+} and Ag^{+} and their Underlying Mechanisms

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Supporting Information File

EXPERIMENTAL SECTION

Synthesis of K-Co-Mo-S_x Gels: K-Co-Mo-S_x wet-gel is synthesized by metathesis route from the reagent grade precursors of K_2S, $(NH_4)_2MoS_4$, I_2, and $Co(NO_3)_2{\cdot}H_2O$ purchased from Millipore sigma following the procedure described elsewhere.[1] The wet-gel was then washed with a mixture of ethanol and water in a ratio of 4:1 twice in a day for two days, then only with ethanol and acetone for two times in day for five days and one day, respectively. Afterward, the gels were dried at ambient temperature to get the xerogel.

Heavy Metal Uptake Experiments: The heavy metal uptake study was conducted for several metal ions M^{n+} (M = Cd, Pb, Cu, Zn, Hg, Ag, and Ni). These experiments were carried out by batch methods for different concentrations and time. The M^{n+} cations, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} were spiked into the deionized water. A solution of deionized water was then interacted with the 10 mg of KCMS xerogel at different time intervals and concentrations. Subsequently, the solutions were centrifuged at 13000 RPM for 30 minutes to precipitate the adsorbents from the heavy metal-contaminated aqueous solutions. The metal ion concentrations in the supernatant solutions were determined using inductively coupled plasma-mass spectrometry (ICP-MS). The post-interacted solid dried gel was analyzed with SEM/EDX and XRD, and XPS.

CHARACTERIZATIONS

X-ray powder diffraction:

X-ray powder diffraction of the powdered gels was conducted in a flat glass sample holder using a Rigaku MiniFlex 600 powder X-ray diffractometer with Ni-filtered Cu $K_{\alpha 1}$ (λ = 1.540593 Å) radiation operating at 40 kV and 20 mA. The measurement was performed with a scan width of 0.02° and a scan rate of 5 °/min and the data was collected from 5 – 80 °(2θ).

Electron Microscopy Imaging and Energy Dispersive Spectroscopy:

A Lyra3 - Tescan scanning electron microscope (SEM) was employed for high-resolution (1.2 nm at 30 keV) imaging and elemental analysis of the samples. During data collection, an accelerating voltage of 20 kV and an accumulation time of 120 seconds were used. Elemental analysis was carried out using the ESED-II (environmental secondary electron detector). The powdered samples were mounted on a carbon-taped metal stub to image the surface morphology of the gels. Samples

were verified by Energy Dispersive Spectroscopy (EDS) and analyzed at a minimum of four spots, with the average composition reported.

Transmission electron microscopy:

The samples were dispersed in acetone by sonication and drop cast on a TEM copper grid. Transmission Electron Microscopy (TEM) analysis was conducted using JEOL1011 at an accelerating voltage of 100kV in TEM imaging mode.

X-ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) spectra of the finely ground powder of the KCMS xerogel were collected using a Thermo Fisher ESCALAB 250Xi spectrometer with an Al-Kα X-ray radiation source, a 500 μm spot size, and an electron flood gun to reduce sample charging. Before each spectra collection, Ar was passed at 30 keV for 30 seconds. Each sample was measured in triplicate, and all spectra were charging shift corrected to the C1s peak at 284.8 eV.

Raman Spectroscopy:

Raman spectroscopy of the post-interacted KCMS gel was collected using a QE65000 spectrometer.

Synchrotron X-ray Pair Distribution Function:

Synchrotron X-ray pair distribution function data was obtained from the 11-ID-B beamline at the Advanced Photon Source (APS) of Argonne National Laboratory. The rapid-acquisition PDF method was used with an X-ray energy of 58.6 k eV ($\lambda = 0.2115$ Å).[2] Sample preparation includes grounding to about the size of 50 μm and then packing in a Kapton capillary. The diffraction

patterns of powder samples of KCMS were collected at room temperature by using rapid acquisition pair distribution function (RA-PDF) technique.[2] The data was integrated using the program Fit2D[3] and corrections, such as subtraction of background and container, Compton, and fluorescence scattering, geometric and adsorption correction, etc.,[4] were performed using the program GSAS-II and PDFgetX3.[5] The normalized data were truncated at 24 $Å^{-1}$ before PDF calculation. GSAS-II and PDFgui were used to model the data.[6,7]

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS):

Heavy metals were analyzed from treated water samples by ICP-MS, model: iCAP RQ, Thermo Fisher Scientific, USA. A Multielement Thermo iCAP RQ tuning solution was used to check the performance test of the instrument. Analytical quality control and calibration curves were produced by using single-element certified reference material from SPEX CertiPrep, USA which is accredited to ISO/IEC 17025 ISO 17034.

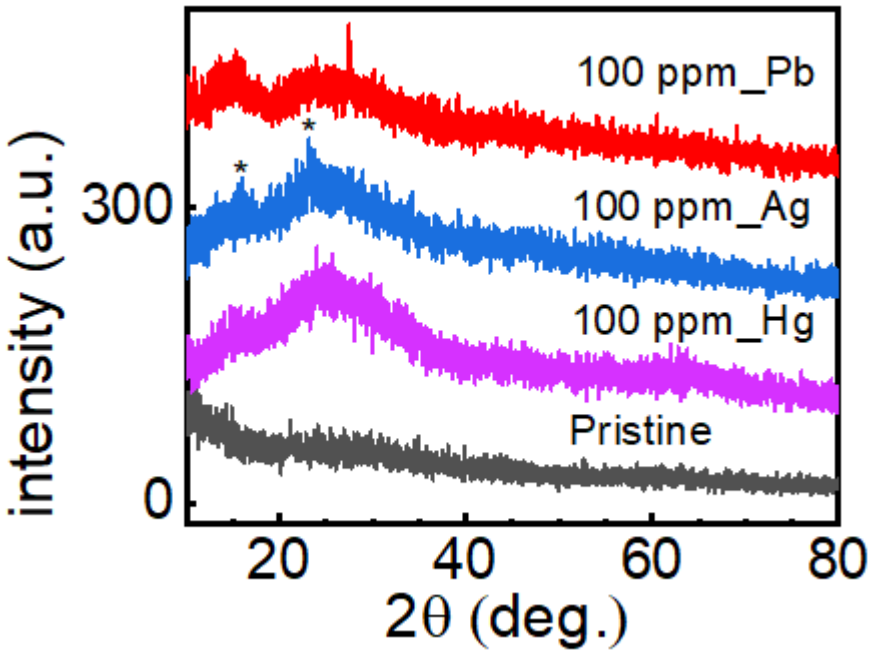

Figure S1. Comparison of XRD patterns of heavy metal (100 ppm) treated KCMS with the pristine material**.**

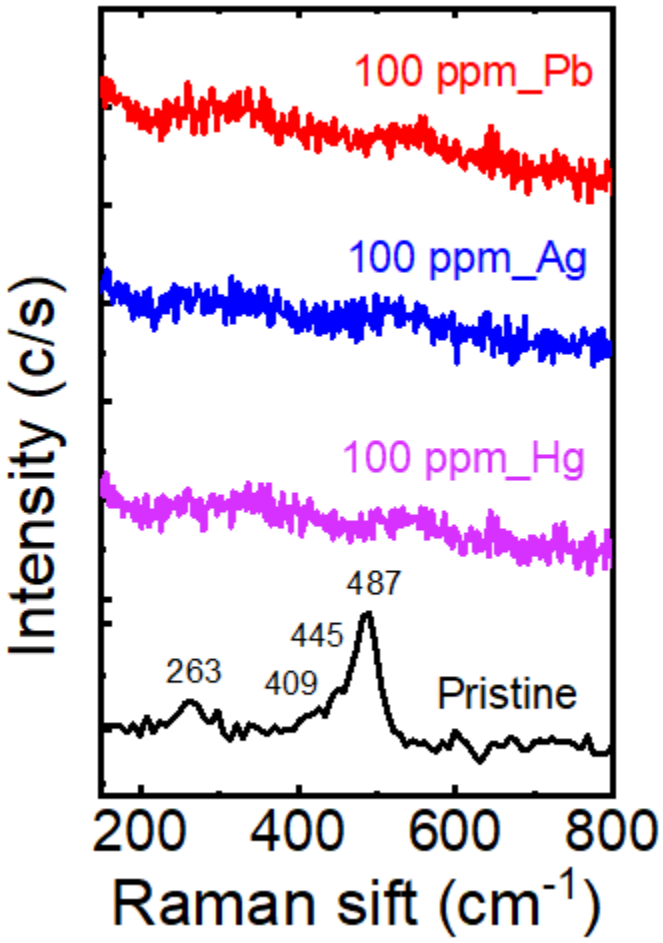

Figure S2. Comparison of Raman spectra of heavy metal (100 ppm) treated KCMS with the pristine material.

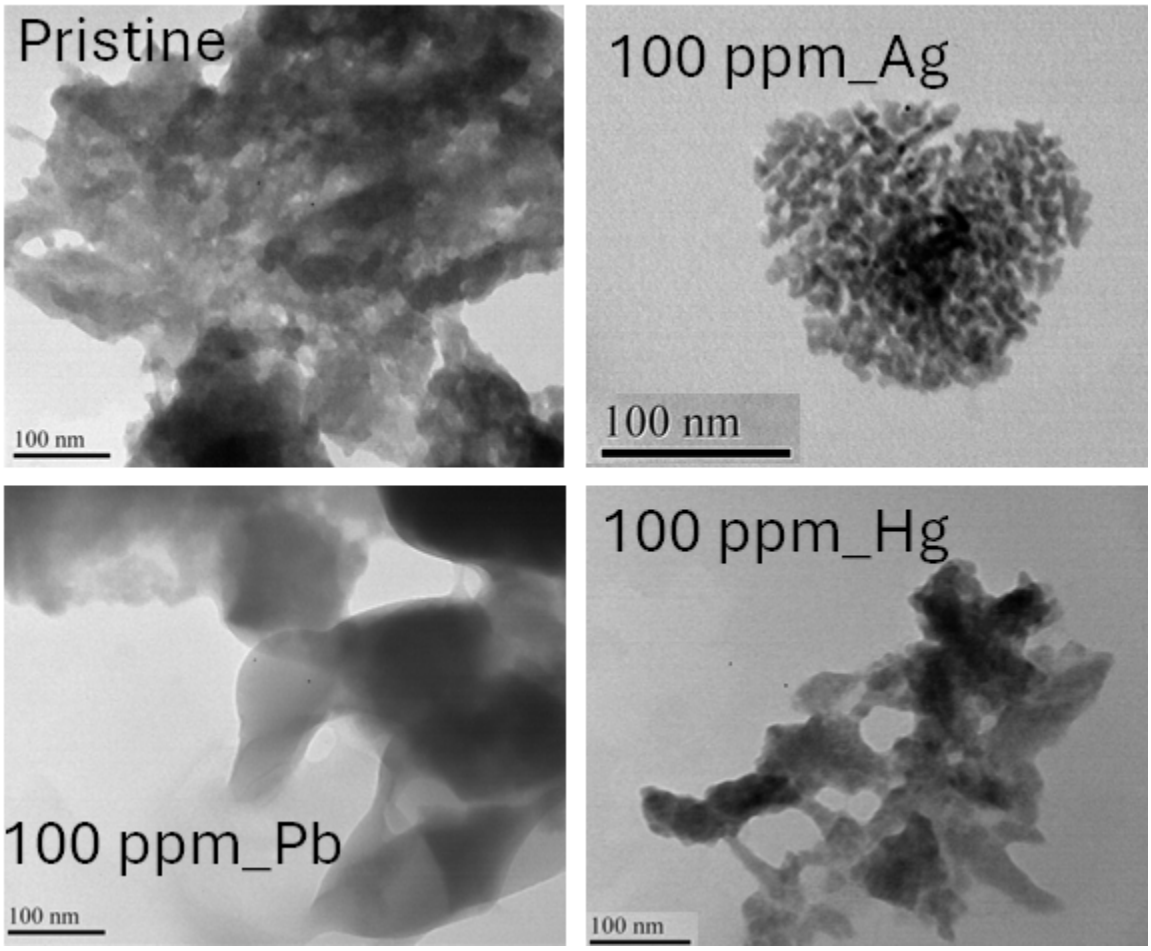

Figure S3. Comparison of TEM images of pristine and post Ag^{+}, Pb^{2+}, and Hg^{2+} (100 ppm) treated KCMS xerogel.

Table S1: Removal of heavy metal cations toward seven **mixed** heavy metal cations in one hour of interactions, (initial concentration: 10 ppm of each, total 70 ppm) by KCMS from wastewater.

M^{n+}	C_i (ppb)	C_f (ppb)	M^{n+} removal (%)	K_d (mL/g)
Cu^{2+}	10×10^3	7.80×10^3	22.00	2.82×10^2
Hg^{2+}	10×10^3	1.30×10^3	87.35	6.91×10^3
Ag^{+}	10×10^3	0.33	~100.00	2.96×10^7
Pb^{2+}	10×10^3	3.92×10^3	62.74	1.68×10^3

Cd^{2+}	10×10^3	10×10^3	0.0	0.0
Ni^{2+}	10×10^3	9.24×10^3	7.6	86.24
Zn^{2+}	10×10^3	10×10^3	0.0	0.0

contact time: 1 h, V = 10.0 mL; *m* (mass of KCMS) =0.01g; V/m ratio=10/0.01=1000 mL/g.

Table S2. Kinetics results for the adsorption Ag^+, Pb^{2+}, and Hg^{2+} by KCMS chalcogel in a single ion state.

Single cations	Time (min.)	C_i (ppb)	C_f (ppb)	SD	M^{n+} removal (%)	SD	K_d (mL/g)	q_t (mg/g)
	5	10×10^3	1822.7	42.28	81.77	0.42	4.49×10^3	8.177
Ag^+	15	10×10^3	11.00	0.57	99.89	0.01	9.08×10^5	9.989
	30	10×10^3	7.85	0.70	99.92	0.01	1.27×10^6	9.992
	60	10×10^3	3.25	1.91	99.97	0.02	3.08×10^6	9.996
	5	10×10^3	48.62	7.14	99.51	0.26	2.04×10^5	9.951
Pb^{2+}	15	10×10^3	2.50	3.39	99.98	0.03	3.99×10^6	9.997
	30	10×10^3	0.10	0.00	100.0	0.00	~10^8	9.999
	60	10×10^3	0.10	0.00	100.0	0.00	~10^8	9.999
	5	10×10^3	1387.8	161.08	86.12	1.61	6.20×10^3	8.700
Hg^{2+}	15	10×10^3	1299.6	497.52	87.00	4.98	6.69×10^3	9.679
	30	10×10^3	320.8	36.06	96.79	0.36	3.01×10^4	9.763
	60	10×10^3	236.8	14.42	97.63	0.14	4.12×10^4	9.999

V = 10.0 ml; *m* (mass of KCMS) =0.01g; V/m ratio=10/0.01=1000 mL/g.

Table S3: Kinetic parameters obtained using the pseudo-second-order rate equation for Ag^+, Pb^{2+} and Hg^{2+}

Parameters	Ag^+	Pb^{2+}	Hg^{2+}
intercept	6.8089×10^{-2}	2.6800×10^{-3}	0.1396
slope	9.8593×10^{-2}	9.9991×10^{-2}	0.1000
R^2	0.999	1	0.999
q_e (mg/g)	10.14	10.00	9.99

q_e^2 $(mg/g)^2$	102.88	100.02	99.82
k_2 $(g/mg \cdot min^{-1})$	1.4×10^{-1}	3.73	7.1×10^{-2}

Table S4. Concentration-dependent removal (%), distribution constant, K_d, and sorption capacity, q_m of heavy metal cations, **Ag^+, Pb^{2+}, and Hg^{2+}** by KCMS gel.

Metal ions	Ci (ppm)	Cf (ppm)	Removal (%)	K_d (mL/g)	q_m (mg/g)
	10	0.0035	99.96	2.84×10^6	10
	50	0.1294	99.74	3.85×10^5	49.87
	100	0.0696	99.86	1.44×10^5	99.93
Ag^+	250	0.2760	99.72	9.05×10^5	249.724
	500	0.5420	93.78	9.21×10^5	499.458
	750	0.526	99.89	1.42×10^6	749.474
	1000	42.224	94.37	2.27×10^4	957.776
	1500	122.328	87.77	1.12×10^4	1377.672
	10	0.0090	99.91	1.10×10^6	9.99
	50	0.3391	99.32	1.46×10^5	49.66
Pb^{2+}	100	0.5064	99.49	1.96×10^5	99.49
	250	44.741	82.10	4.59×10^3	205.26
	500	173.60	65.28	1.88×10^3	326.40
	1000	561.26	43.87	7.81×10^2	438.74
	1500	477.23	68.18	2.14×10^3	1022.77
	3000	1853.81	38.21	6.18×10^2	1146.19
	10	0.0095	99.91	1.05×10^6	9.99
	50	0.2732	99.45	1.82×10^5	49.72
	100	0.4382	99.56	2.72×10^5	99.56
Hg^{2+}	250	8.026	96.79	3.01×10^4	241.97
	500	316.174	56.77	1.31×10^3	283.83
	1000	539.432	46.06	8.53×10^2	460.57
	1500	1047.252	30.18	4.32×10^2	452.75

contact time: 1 h, V = 10.0 mL; *m* (mass of KCMS) =0.01g; V/m ratio=10/0.01=1000 mL/g

Table S5. Average EDS compositions of the post-interacted KCMS gel spiked with different concentrations of Pb^{2+} ions, compositions are in atomic percentage.

KCMS	S-K	K-K	Co-K	Mo-L	Pb-L
Pristine	67.42	12.59	9.57	10.42	
Pb^{2+} 100 ppm_pt1	71.23	0	6.87	14.51	7.39
Pb^{2+} 100 ppm_pt2	77.36	0	3.03	11.33	8.29

Pb^{2+} 100 ppm_pt3	78.1	0.09	2.29	13.45	6.07
Pb^{2+} 100 ppm_pt4	78.97	0.34	5.37	9.07	6.26
Average	**76.42**	**0.11**	**4.39**	**12.09**	**7.00**
Pb^{2+} 2000 ppm_pt1	44.49	0.19	0.26	13.38	41.68
Pb^{2+} 2000 ppm_pt2	38.24	0.15	0.04	19.3	42.27
Pb^{2+} 2000 ppm_pt3	67.47	0.09	0.18	8.2	24.07
Pb^{2+} 2000 ppm_pt4	52.77	0.11	0.31	12.61	34.2
Average	**50.74**	**0.14**	**0.20**	**13.37**	**35.56**

Table S6. Average EDS compositions of the post-interacted KCMS gel spiked with different concentrations of Ag^{+} ions, compositions are in atomic percentage.

KCMS	S-K	K-K	Co-K	Mo-L	Ag-L
Pristine	67.42	12.59	9.57	10.42	
Ag^{+} 100 ppm pt1	75.93	0.15	2.45	10.78	10.69
Ag^{+} 100 ppm pt2	76.68	0.01	3.93	10.81	8.56
Ag^{+} 100 ppm pt3	76.12	0	4.42	10.19	9.27
Ag^{+} 100 ppm pt4	65.02	0	3.04	10.69	21.24
Average	**73.44**	**0.04**	**3.46**	**10.62**	**13.02**
Ag^{+} 1500 ppm_pt1	60.24	0	1.48	7.62	30.66
Ag^{+} 1500 ppm pt2	57.81	0	2.28	8.73	31.18
Ag^{+} 1500 ppm pt3	58.18	0	3.02	7.77	31.03
Ag^{+} 1500 ppm pt4	56.04	0	2.72	8.15	33.08
Average	**58.07**	**0**	**2.38**	**8.07**	**31.49**

Table S7. Average EDS compositions of the post-interacted KCMS gel spiked with different concentrations of Hg^{2+} ions, compositions are in atomic percentage.

KCMS	S-K	K-K	Co-K	Mo-L	Hg-L
Pristine	67.42	12.59	9.57	10.42	
Hg^{2+} 100 ppm_pt1	81.93	0	6.03	5.4	6.64
Hg^{2+} 100 ppm_pt2	85.51	0	4.8	5.53	4.15
Hg^{2+} 100 ppm_pt3	84.51	0	5.94	5.71	3.84

Hg^{2+} 100 ppm_pt4	85.14	0	5.18	5.99	3.68
Average	**84.27**	**0.00**	**5.49**	**5.66**	4.58
Hg^{2+} 1000 ppm_pt1	81.8	0	2.79	6.66	8.75
Hg^{2+} 1000 ppm_pt2	82.82	0.02	2.16	3.56	11.44
Hg^{2+} 1000 ppm_pt3	67.29	0	2.03	1.06	29.62
Hg^{2+} 1000 ppm_pt4	76.56	0	2.84	4.08	16.52
Average	**75.56**	**0.01**	**2.46**	**3.84**	**16.58**

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