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

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## ABSTRACT

Chalcogenide-based aerogels, known as chalcogels, represent a novel class of nanoparticle-based porous amorphous materials characterized by high surface polarizability and Lewis base properties, exhibiting promising applications in clean energy and separation science. This work presents K-Co-Mo-$S_x$ (KCMS) chalcogel as a highly efficient sorbent for heavy metal ions and details its sorption mechanisms. Its incoherent structure comprises $Mo_2^{V}(S_2)_6$ and $Mo_3^{IV}S(S_6)_2$ anion-like clusters with four- and six-coordinated Co─S polyhedra, forming a Co-Mo-S covalent network that hosts $K^+$ ions through electrostatic attraction. Interactions of KCMS with heavy metal ions, particularly $Pb^{2+}$ and $Ag^+$, revealed that KCMS is exceptionally effective in removing these ions from ppm concentrations down to trace levels (≤5 ppb). KCMS rapidly removes $Ag^+$ (≈81.7%) and $Pb^{2+}$ (≈99.5%) within five minutes, achieving >99.9% removal within an hour, with a distribution constant, $K_d \geq 10^8$ mL/g. KCMS exhibits an impressive removal capacity of 1378

mg/g for $Ag^{+}$ and 1146 mg/g for $Pb^{2+}$, establishing it as one of the most effective materials known to date for heavy metal removal. This material is also effective for the removal of $Ag^{+}$ and $Pb^{2+}$ along with $Hg^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Cd^{2+}$ from various waters even in the presence of highly concentrated and chemically diverse cations, anions, and organic species. Analysis of the post-interacted KCMS by synchrotron X-ray pair distribution function (PDF), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) revealed the sorption of $Pb^{2+}$, $Ag^{+}$, and $Hg^{2+}$ mainly occurs by the exchange of $K^{+}$ and $Co^{2+}$. Despite being amorphous, this material exhibits unprecedented ion-exchange mechanisms both for the ionically and covalently bound $K^{+}$ and $Co^{2+}$, respectively. This discovery advances our knowledge of amorphous gels and guides material synthesis principles for the highly selective and efficient removal of heavy metal ions from water.

**Keywords:** chalcogels, heavy metal remediation, wastewater, ion-exchange

**Synopsys:** Disordered aggregated porous nanoparticles of KCMS are highly efficient and have exceptionally high sorption capacity in removing silver and lead cations following the exchange of potassium and cobalt cations bonded electrostatically and covalently in KCMS, respectively.

## INTRODUCTION

The industrial revolution has substantially accelerated the demand for indiscriminate exploitation of global resources, thereby worsening environmental crises worldwide.[1] Among the array of industrial pollutants, heavy metal-containing wastewater remains a focal concern because of their improper handling and disposal leading to their release into water and subsequent contamination of the ecosystem. Heavy metals are generally harmful to biological systems, including humans, with certain ones such as lead, mercury, silver, and cadmium posing significant risks, including carcinogenicity, neurocognitive disorders, and DNA damage to human health even at trace levels.[2–7] Hence, it is of utmost importance to decontaminate wastewater containing heavy metals before discharging it into the environment.

In recent years, numerous methods, such as electrocoagulation (EC),[8] adsorption,[9,10] membrane separation,[10,11] magnetic field implementations,[12] electrokinetic extraction,[13] ion-exchange[14] and others were introduced to remove heavy metals from water. Among the various chemical approaches, ion exchange is potentially viable for the decontamination of water because of its superiority in selectivity and efficiency in separating heavy metal ions from wastewater.[15–18] Different materials, such as zeolite, activated carbon, biochar, polymer, biomaterials, resin, and layered double hydroxides have been used for heavy metals removal.[19–25] While these materials demonstrate some degree of effectiveness in separating numerous heavy metals, they often exhibit poor selectivity, efficiency, sorption kinetics, and capacity. Also, their shortcomings become evident when addressing the challenge of removing heavy metals at trace levels from water.

Sulfur-based materials exhibit superior affinity towards heavy metal ions[26] and possess the capability to selectively bind Lewis acidic soft heavy metal ions, following Pearson's hard-soft Lewis acid-base principles (HSAB).[27] Consequently, this class of materials has emerged as efficient sorbents for soft heavy metal cations, such as $Hg^{2+}$, $Pb^{2+}$, $Ag^{+}$, $Cu^{2+}$, and $Cd^{2+}$ enabling their selective separation even at trace levels. In recent years, chemically and structurally diverse metal sulfides have been investigated in removing soft or relatively soft heavy metal cations. These materials include layered metal sulfides: $K_{2x}Mn_xSn_{3-x}S_6$ (KMS-1),[15,28] $H_{2x}Mn_xSn_{3-x}S_6$ (LHMS-1),[29] $K_{2x}Mg_xSn_{3-x}S_6$ (KMS-2),[16] $K_{2x}Sn_{4-x}S_{8-x}$ (KTS-3),[17] open framework structures, such as $K_6Sn[Zn_4Sn_4S_{17}]$,[30] $[(Me)_2NH_2]_2[GeSb_2S_6]$,[31] metal sulfide intercalated layered double hydroxides, and chalcogels.[32,33]

Among them, chalcogel, an emerging class porous nanoparticle-based amorphous materials, stands out remarkably because of its unique structural skeleton consisting of polysulfides, which finds great affinity toward chemically soft Lewis acidic cations.[34–36] Structurally, chalcogels typically comprise monomeric units of (metal-)chalcogenides, interconnected through either chalcogen-chalcogen or metal-chalcogenide covalent bonds and thus integrate high-density (poly)sulfide into its nanoparticles. Hence, the incorporation of alkali metals into the covalent networks of metal-sulfide can introduce electrostatic bonding features. This leads to the formation of hybrid chalcogels consisting of covalent and ionic bonds. This can represent a distinct class of porous nanomaterials with ion-exchange properties akin to crystalline metal sulfides, including $K_{2x}M_xSn_{3-x}S_6$ (M = Mn, KMS-1; M = Mg, KMS-2),[15,16] $K_{2x}Sn_{4-x}S_{8-x}$ (x = 0.65–1),[17] and

$K_6Sn_5Zn_4S_{17}$[30] which shows ion-exchange properties toward chemically soft Lewis acidic heavy metal ions.[37] This characteristic holds promise for potential applications in wastewater treatment and the extraction of critical metals from water sources.

Here, we present the significant potential of K-Co-Mo-$S_x$ chalcogel for effectively separating heavy metal cations from aqueous solutions. This material exhibits over 99.9% removal of $Ag^+$ and $Pb^{2+}$ from initial concentrations of about $10^4$ ppb, with the distribution constants of $K_d \geq 10^8$ mL/g in just an hour. Besides, KCMS exhibits an enormously high sorption capacity of $q_m^{Ag} \sim 1378$, $q_m^{Pb} \sim 1146$, and also for mercury, $q_m^{Hg} \sim 461$ mg/g. Moreover, KCMS can remove $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ from ppm to trace level ($\leq 5$ ppb) from naturally contaminated wastewater systems. Despite being amorphous, this material exhibits double ion-exchange properties for ionically and covalently bound $K^+$ and $Co^{2+}$, respectively. Overall, the integration of rapid, high-capacity removal of heavy metals, alongside room temperature-scalable synthesis and an unprecedented adsorption mechanism, demonstrates the transformative potential of chalcogels in wastewater treatment.

## RESULTS AND DISCUSSIONS

**Synthesis and characterization:** K-Co-Mo-$S_x$ chalcogel was synthesized via a redox-driven metathesis route in solution at room temperature, following a previously reported procedure (detailed in the SI).[38] After the synthesis of the wet-gel, the as-prepared gel in the solution was washed to remove the unreacted spectator ions (Figure 1A). The gel was then dried at room temperature to produce xerogel. Scanning electron microscopy (SEM) images of the xerogel show

105 homogeneity of the gel particle (Figure 1B). As discussed previously, detailed analysis of the
106 chemical composition by SEM/EDS analysis of the K-Co-Mo-S chalcogel, synthesized from
107 various batches was collected in micrometer length scales, indicating an average atomic abundance
108 of K, Co, Mo, and S as 8.0±2.3, 7.4±1.7, 9.4±1.6, and 74.2±4.6%, respectively and are closely
109 related to results obtained from submicron-level particles determined by TEM/EDS.[38] The absence
110 of any sharp diffraction peak in the XRD pattern of the KCMS gels suggests the lack of periodic
111 arrangement in its amorphous structure (Figure 1C). Synchrotron X-ray pair distribution functions
112 analysis shows peaks at 2.03, 2.42, and 2.73Å which are related to S-S, Mo-S, and Mo-Mo bonding
113 correlations, respectively (Figure 1D). This finding is akin to the previously reported results.[38]
114 Previously, we elucidated the local coordination environment of KCMS gels by XPS, HRTEM,
115 TEM-EDS, XANES, and EXAFS analysis.[38] Modeling of the Co and Mo K-edges data revealed
116 that six- and four-coordinated Co─S polyhedra linked with Mo─S anionic clusters resembling
117 molecular $Mo_2^{V}(S_2)_6$ and $Mo_3^{IV}S(S_6)_2$ anions.[38] We found that KCMS nanoparticles consist of
118 covalent networks of the Co-Mo-S in which $K^+$ ions are electrostatically bound to form K-Co-Mo-
119 $S_x$ chalcogel. Hence, the presence of electrostatically bound alkali metals in the covalent network
120 of the Co-Mo-S of the KCMS gels can be ion-exchanged with chemically soft heavy metal cations
121 following the Lewis HSAB principles.[27]

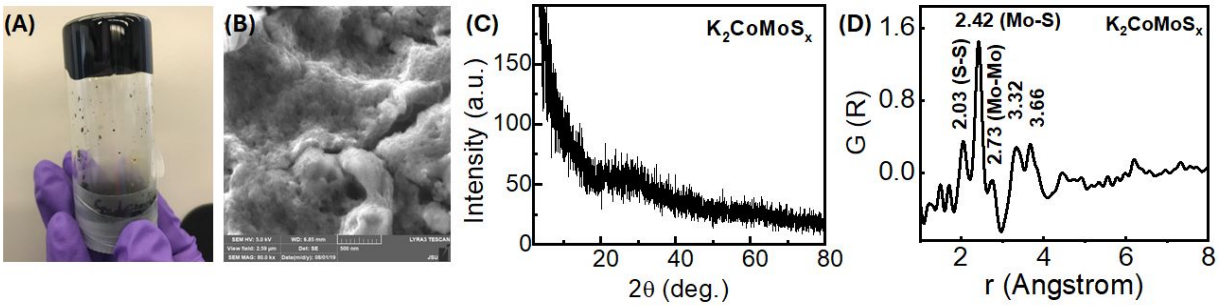



**Figure 1**. Photograph of the KCMS wet gels (upside down) showing the firmness of the monolith wet gels (A), SEM image of the KCMS xerogel (B), XRD pattern of KCMS xerogel showing amorphous nature of the material (C), PDF analysis of KCMS xerogel demonstrates a short rage atomic order with the local coordination of polyhedra (D).

**Extraction of Heavy Metal Ions from Aqueous Solutions:** We investigated the interactions of the xerogels of KCMS, obtained by drying at ambient conditions, with various transition metal cations that include $Cu^{2+}$, $Hg^{2+}$, $Ag^{+}$, $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ (Table 1). Our studies reveal that KCMS is remarkably efficient for the capture of $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$ from aqueous solutions. KCMS achieves nearly 100% removal of $Ag^{+}$ and $Pb^{2+}$ in an interaction time of just about an hour with the distribution constant, $K_d$ as high as ~$10^8$ mL/g from 10 ppm spiked solutions of metal cations. It also shows effective removal efficiencies for $Cu^{2+}$ and $Hg^{2+}$, offering removal of ~91 and 98%, respectively, with a $K_d > 10^4$ mL/g (Table 1). Such high $K_d$ values suggest a great affinity of the $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$ for the KCMS chalcogel. It is important to note that any materials with a $K_d$ value in the $10^4$–$10^5$ mL/g range are regarded as exceptionally high-quality sorbents.[17,39] It is important to note that the aerogel form of KCMS which exhibits a surface area of up to 90 $m^2$/g, as reported previously,[38] could potentially be more effective due to its high density of pores across the aggregated nanoparticles. However, due to the challenges associated with scalable and cost-

effective synthesis, this study focuses solely on the xerogel form of KCMS.

**Table 1:** Removal of various heavy metal cations from aqueous solutions by KCMS.

| $M^{n+}$ | $C_i$ (ppm) | $C_f$ (ppb) | $M^{n+}$ removal (%) | $K_d$ (mL/g) |
|---|---|---|---|---|
| $Cu^{2+}$ | $10\times10^3$ | 872.0 | 91.30 | $1.05\times10^4$ |
| $Hg^{2+}$ | $10\times10^3$ | 236.8 | 97.63 | $4.12\times10^4$ |
| $Ag^{+}$ | $10\times10^3$ | 3.25 | 99.97 | $3.08\times10^6$ |
| $Pb^{2+}$ | $10\times10^3$ | 0.10 | ~100.0 | $\sim10^8$ |
| $Cd^{2+}$ | $10\times10^3$ | $9.91\times10^3$ | 0.86 | 8.65 |
| $Ni^{2+}$ | $10\times10^3$ | $9.12\times10^3$ | 8.8 | 96.49 |
| $Zn^{2+}$ | $10\times10^3$ | $10\times10^3$ | 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.

The competitive sorption analysis of heavy metal cations by KCMS xerogels revealed that only in one hour of interaction, the final concentration of silver ion was reduced from 10,000 to below one ppb, demonstrating an excellent potential of the gels for fast and efficient removal of $Ag^{+}$ from aqueous solutions (Table S1). Other heavy metal cations, e.g. $Hg^{2+}$, and $Pb^{2+}$, show reasonably good sorption efficiency, whereas other ions show poor to negligible interactions to separate them from water. Based on this result, we found the selectivity order as $Ag^{+} > Hg^{2+} > Pb^{2+} >> Cu^{2+} >> Ni^{2+} >> Cd^{2+}$. This finding suggests that KCMS is effective for the selective separation of different heavy metal cations as listed above. This kind of selectivity may be understood by the chemical hardness of these cations. This is because of different binding propensities to chemically soft Lewis basic sulfides of the KCMS with heavy metal ions, as demonstrated by Pearson's Lewis hard and soft acid-base principle.[27] This observation is in good agreement with the previously reported

investigation.[40]

Time-dependent experiments for the sorption of $Ag^+$, $Pb^{2+}$, and $Hg^{2+}$ were conducted for KCMS xerogel to determine the removal rate of these metal cations and to understand the mechanism of sorption (Figure 2). The sorption kinetic for $Pb^{2+}$ is ultra-fast. The removal rate of $Pb^{2+}$ cations from the $10^4$ ppb spiked solution is 99.51% in 5 minutes and reaches ~100% within 30 min with a $K_d$ value of ~$10^8$ mL/g and the final concentration of those heavy metal cations reached < 1 ppb (ng/g). Importantly, such a low concentration for $Pb^{2+}$ is well below the limit for drinking water defined by both the US EPA (15 ppb) and WHO (10 ppb).[41,42]

Furthermore, the removal of $Ag^+$ and $Hg^{2+}$ reaches about 81.7% and 86.1%, respectively, within 5 minutes and increases to ~ 97.6% ($K_d$ ~ $3.8\times10^6$ mL/g) and 97.6% ($K_d$ ~ $4\times10^4$ mL/g) within an hour (Table S2). This kind of exceedingly high uptake rate adverts KCMS's potential for the rapid decontamination of $Ag^+$, $Pb^{2+}$, and $Hg^{2+}$ from wastewater. In general, sorption rates and mechanisms can be analyzed by pseudo-first and pseudo-second-order rate equations as described in equations 1 and 2, respectively.[43]

$$\text{Pseudo-first-order: } \ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{(eq. 1)}$$

$$\text{Pseudo-second-order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(eq. 2)}$$

Where $q_e$ (mg/g) is the amount of adsorbed element per unit mass of adsorbent at equilibrium and $q_t$ (mg/g) is the adsorbed amount at time $t$, while $k_1$ ($min^{-1}$) and $k_2$ ($g/mg\cdot min^{-1}$) are equilibrium rate constants of pseudo-first-order and pseudo-second-order adsorption interactions, respectively.[44] Fitting of the experimental data led to a decent linear relationship for the '$t/q_t$' versus '$t$' plot (Figure 2D), demonstrating the sorption of $Ag^+$, $Pb^{2+}$, and $Hg^{2+}$ follow the pseudo-

second-order rate equations where the rate constant, $k_2$, for $Pb^{2+}$ is ~ 3.73 g/mg·min$^{-1}$, which is about one and two orders of magnitude higher than that for $Ag^{+}$ ($k_2^{Ag}$ ~ 0.14 g/mg·min$^{-1}$) and $Hg^{2+}$ ($k_2^{Hg}$ ~0.071 g/mg·min$^{-1}$), respectively. (Table S3). Such a higher rate constant is indicative of faster sorption of these ions and agrees with the experimental data (Table S2). The correlation coefficients ($R^2$) were nearly equal to unity suggesting that KCMS follows pseudo-second-order reaction kinetics for the interactions with $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$.

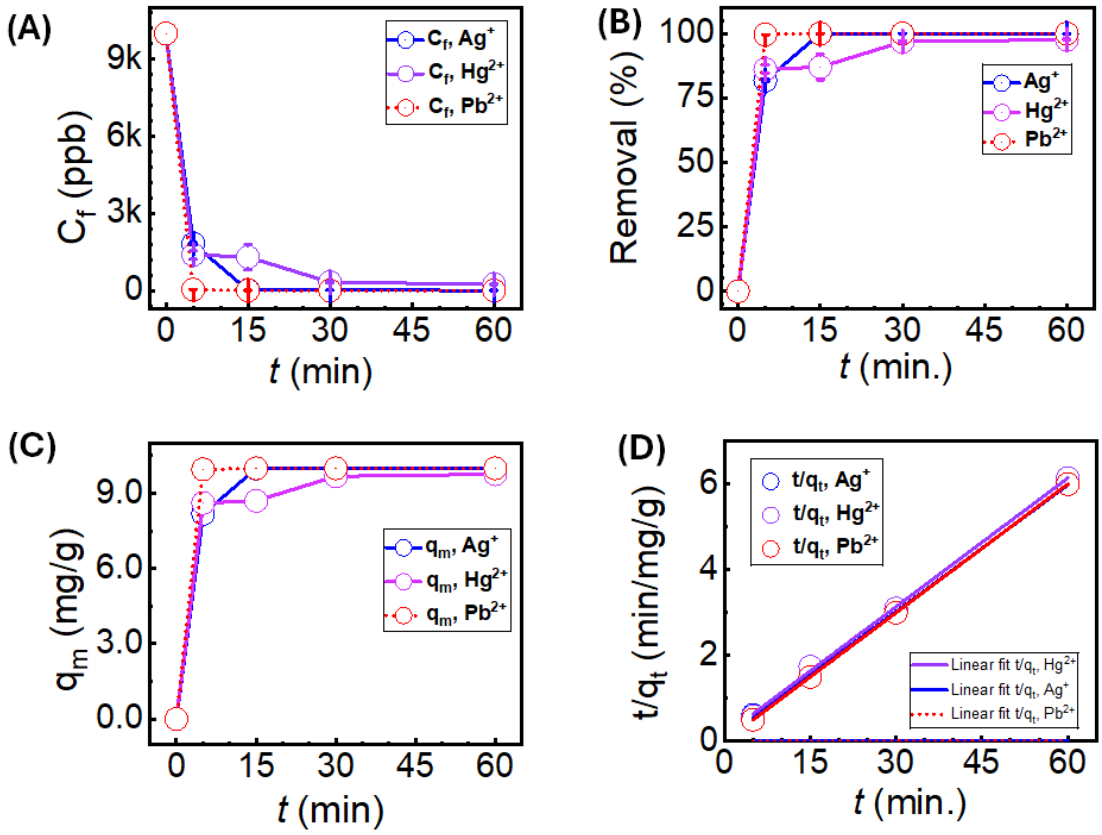
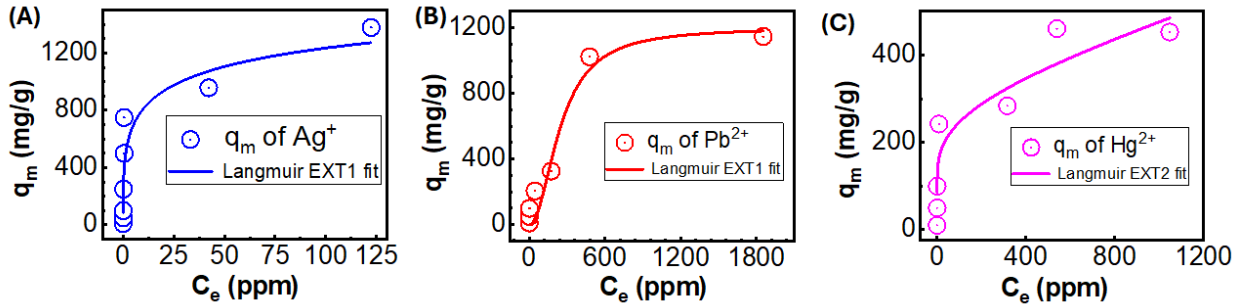



**Figure 2.** Sorption kinetic for $M^{n+}$ ($Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$) using 10.0 mg of KCMS xerogel in 10 mL of solution: (A) change of [$M^{n+}$] to the time of interactions, (B) removal % of $M^{n+}$ as a function of time, (C) sorption capacity as a function of contact time, and (D) pseudo-second-order kinetic plots.

To determine the sorption capacity of the KCMS xerogel for $Hg^{2+}$, $Ag^{+}$, and $Pb^{2+}$ in aqueous solutions, we conducted a concentration investigation and fitted the experimental data with the Langmuir adsorption isotherms model (Figure 3, Table S4). This investigation reveals that KCMS has a remarkably high sorption capacity for $Hg^{2+}$, $Ag^{+}$, and $Pb^{2+}$. Our investigations show that KCMS can capture over 87% of $Ag^{+}$ from a concentration as high as 1500 ppm with a $K_d$ value of $1.4\times10^4$ mL/g (Table S4). At this concentration, the maximum sorption capacity was determined to be ~1377 mg/g (Figure 3A) where the sorption data were nicely fitted with Langmuir absorption isotherm. This value of $q_m^{Ag}$ is exceptionally high, and stands out as one of the most efficient sorbents among the top materials, such as LDH-$Mo_3S_{13}$ (1073 mg/g),[45] amorphous $MoO_x$ (2605 mg/g),[46] LDH-$Sn_2S_6$ (978 mg/g),[39] LDH Ni/Fe/Ti-$MoS_4$-LDH (856 mg/g),[47] Mn-$MoS_4$ (564 mg/g),[48] LDH-$MoS_4$ (550 mg/g),[49] $MoS_4$-ppy (480 mg/g at pH ~5),[50] and $Mo_3S_{13}$-Ppy (408 mg/g) (Table 2).[51] In addition, our experiment shows that KCMS can remove over 99.5 % of $Pb^{2+}$ with starting concentrations over 100 ppm. The maximum removal capacity of 1146 mg/g was obtained for a spiked solution of 3000 ppm (Figure 3B). Such a tremendously high sorption capacity for $Pb^{2+}$ ranks this material top among the other high-performing $Pb^{2+}$ sorbents, as we can see in Table 2.[48,49,52–57] We have also investigated the adsorption capacity of $Hg^{2+}$ for solutions of 10 to 1500 ppm. The KCMS affords the removal capacity, $q_m^{Hg}$ ~ 460 mg/g (Figure 3C) which is comparable to other high-performing sorbents as seen in (Table 2). Importantly, KCMS can remove ≥ 99.6% $Hg^{2+}$ from a solution containing as high as 100 ppm of $Hg^{2+}$ (Table S4). Over these concentration ranges (10-100 ppm), the $K_d^{Hg}$ values remain in the range of $10^5$-$10^6$ mL/g. Such an exceedingly high $K_d$ demonstrates that KCMS offers paramount potential in the removal of $Hg^{2+}$ from aqueous

211 solutions.




212

213 Figure 3. The sorption capacity of heavy metal cations, $Ag^+$ (A), $Pb^{2+}$ (B), and $Hg^{2+}$ (C) by KCMS
214 chalcogel was determined by the interaction of 10 mg KCMS with various concentrations of each
215 cation.

216

217 Table 2: Comparison of adsorption capacities for heavy metals with high-performing sorbents
218

| Cations | Adsorbents | $q_m$ (mg/g) | References |
|---|---|---|---|
| **$Ag^+$** | **KCMS** | **1377** | **This work** |
| | Amorphous $MoO_x$ | 2605 | 46 |
| | LDH-$Mo_3S_{13}$ | 1074 | 45 |
| | LDH-$Sn_2S_6$ | 978 | 39 |
| | Ni/Fe/Ti–$MoS_4$-LDH | 856 | 47 |
| | Mn-LDH-$MoS_4$ | 564 | 48 |
| | $MoS_4$-Ppy | 480 (pH~5)<br>725 (pH ~1) | 50 |
| | $Mo_3S_{13}$-ppy | 408 | 51 |
| | $MoS_4$-LDH | 450 | 49 |
| | KMS-2 | 408 | 58 |
| | Fe-$MoS_4$ | 565 | 52 |
| **$Pb^{2+}$** | **KCMS** | **1146** | **This work** |
| | Lignosulfonate-modified graphene hydrogel | 1210 | 59 |
| | LDH-$Sn_2S_6$ | 579 | 39 |
| | $MoS_4$-LDH | 290 | 49 |
| | Mn-$MoS_4$ | 357 | 48 |
| | Fe-$MoS_4$ | 345 | 52 |
| | EDTA-LDH | 180 | 54 |

| | | | |
|---|---|---|---|
| | CTS/PAM gel | 138 | [55] |
| | $Mg_2Al$-LS-LDH | 123 | [56] |
| | Cellulose-based chalcogel | 240 | [57] |
| | biomass-based hydrogel | 422.7 | [53] |
| **$Hg^{2+}$** | **KCMS** | **460** | **This work** |
| | LDH-$Sn_2S_6$ | 666 | [39] |
| | $MoS_4$-LDH | 500 | [49] |
| | Mn- $MoS_4$ | 594 | [48] |
| | Fe-$MoS_4$ | 582 | [52] |
| | KMS-2 | 297 | [58] |
| | $MoS_4$-ppy | 210 | [50] |
| | KMS-1 | 377 | [29] |
| | Thio-functionalized magnetic graphene oxide | 289 | [60] |

**Application Potentials:** To evaluate the practical use of KCMS xerogel chalcogel for wastewater treatment, we analyzed its removal efficiency for heavy metals using Mississippi River Water (MRW) and Tap Water (TW). Water from both sources was individually spiked with 10 ppm of each metal as listed, $Ag^+$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Cd^{2+}$, resulting in a total concentration of 70 ppm for seven metal ions. Despite the presence of chemically diverse types of species, including high concentrations of cations, anions, and diverse organic species, in those water samples, KCMS can remove $Ag^+$, $Hg^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Cd^{2+}$ (Table 3). Specifically, the removal performance of $Ag^+$ and $Pb^{2+}$ from MRW is over 99% and leads to the final concentration of less than 1 ppb. We obtained the selectivity order for tap and Mississippi River water to be $Ag^+ \approx Pb^{2+} > Hg^{2+} > Cu^{2+} >> Cd^{2+} > Ni^{2+}$. This finding suggests that KCMS possesses extraordinary potential for the selective separation of $Ag^+$ and $Pb^{2+}$ from contaminated waters and thus could be useful for the selective extraction of $Ag^+$ and $Pb^{2+}$ from wastewater.

**Table 3.** Sorption results of KCMS in potable Tap water and Mississippi river water containing seven metal ions of 10 ppm for each (70 ppm total), $C_i$ = initial (pre-sorption) concentration, $C_f$ =final (post-adsorption) concentration.

| Mixed-ions | $C_i$ (ppm) | $C_f$ (ppm) | Removal (%) | $K_d$ (mL/g) | $q_m$ (mg/g) | $C_f$ (ppm) | Removal (%) | $K_d$ (mL/g) | $q_m$ (mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | | | **Tap water** | | | | **MRW** | | |
| $Cu^{2+}$ | 10.0 | 3.6184 | 63.81 | 1782.4 | 6.381 | 3.1254 | 68.74 | $2.22\times10^{3}$ | 6.874 |
| $Hg^{2+}$ | 10.0 | 0.2132 | 97.86 | $4.60\times10^{4}$ | 9.786 | 0.1749 | 98.25 | $5.68\times10^{4}$ | 9.825 |
| $Ag^{+}$ | 10.0 | 0.0336 | 99.66 | $2.96\times10^{5}$ | 9.966 | 0.0524 | 99.48 | $2.08\times10^{5}$ | 9.948 |
| $Pb^{2+}$ | 10.0 | 0.0686 | 99.31 | $1.51\times10^{5}$ | 9.931 | 0.0279 | 99.72 | $3.4\times10^{7}$ | 9.972 |
| $Cd^{2+}$ | 10.0 | 8.0149 | 19.85 | 258.65 | 1.985 | 8.1857 | 18.14 | $2.30\times10^{2}$ | 1.814 |
| $Ni^{2}$ | 10.0 | 9.5000 | 4.64 | 48.63 | 0.463 | 9.3766 | 6.23 | $6.63\times10^{1}$ | 0.623 |
| $Zn^{2+}$ | 10.0 | 10 | 0.0 | 0.0 | 0.0 | 10.0 | 0.0 | 0.0 | 0.0 |

contact time: 24 h, V = 10.0 mL; *m* (mass of KCMS) =0.01g; V/m ratio=10/0.01=1000 mL/g

**Mechanistic Insights into the Interactions of KCMS with $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$:** To evaluate the sorption mechanisms of $M^{n+} \equiv Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$ ions by KCMS gels, we analyzed the post-reacted sorbent by XRD, PDF, EDS, and XPS. The XRD of the KCMS after interactions with 100 ppm of $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$ cations showed the material remains amorphous (Figure S1). The XRD of the post-interacted materials primarily revealed their amorphousness similar to the pristine KCMS. However, the $Ag^{+}$ interacted samples showed weak peak-like humps at 2Θ ~15.5 and 23.0$^{o}$, which could not be identified. We further analyze the post-treated material by Raman, and TEM for deeper understanding. The strong Raman shift of the pristine KCMS at 487 $cm^{-1}$ (and the shoulder at ~ 445 $cm^{-1}$ ) and weak shift at 263 $cm^{-1}$ are attributed to the polysulfide species and K-

S bond, respectively[38] being missing in the 100 ppm $Hg^{2+}$, $Ag^{+}$, and $Pb^{2+}$ treated material (Figure S2) indicating the ion-exchange and Ag─S─*M*, Pb─S─*M*, and Hg─S─*M* (*M*=Mo, Co) like interactions. Besides, the TEM images of the $Hg^{2+}$ and $Ag^{+}$ (Figure S3) interacted samples show the aggregation of the particles as expected to the pristine materials. In contrast, the $Pb^{2+}$ interacted sorbent showed a platelike pattern, however, XRD does not reveal the crystalline of the sorbent. Analogous to the pristine KCMS, the PDF of the post-interacted KCMS shows local atomic ordering up to about 6 Å (Figure 4). PDF of KCMS after interactions with 100 ppm of $Ag^{+}$ and $Pb^{2+}$ show a decrease in intensity of the peak at 3.7 Å which is relevant to K⋯S correlations. Such a reduction in intensity of the 3.7 Å peak can be attributed to a lower concentration of the $K^{+}$ ions in the networks of the KCMS gels suggesting the exchange of $K^{+}$ with $Ag^{+}$ and $Pb^{2+}$. Besides, PDF also shows a decrease in the intensity of $S_n^{2-}$ correlated peaks at ~ 2.0 Å after interactions with $Ag^{+}$ and $Pb^{2+}$ ions. This is due to the breakdown of the S─S bonds of the polysulfide species of the surface exposed chalcogels particles through the formation of Ag─S─M and Pb─S─M bonds, where M is Co or Mo of the KCMS. This finding suggests that besides the ion exchange of $K^{+}$ by $Ag^{+}$ and $Pb^{2+}$, covalent interactions of $Ag^{+}$ and $Pb^{2+}$ with the $(\text{─S─S─})_n$ species of the gel nanoparticles, as ─S─Ag/Pb─ attribute the sorption of these cations. Besides, although the PDF demonstrates the stability of the KCMS gel's first coordination sphere, the structural changes after sorbent interactions cannot be fully verified due to its amorphous nature. It is also important to note that the sorption of $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$ is irreversible, which can be attributed to the stronger *M*-S (*M* = $Ag^{+}$, $Pb^{2+}$, $Hg^{2+}$) covalent interactions.

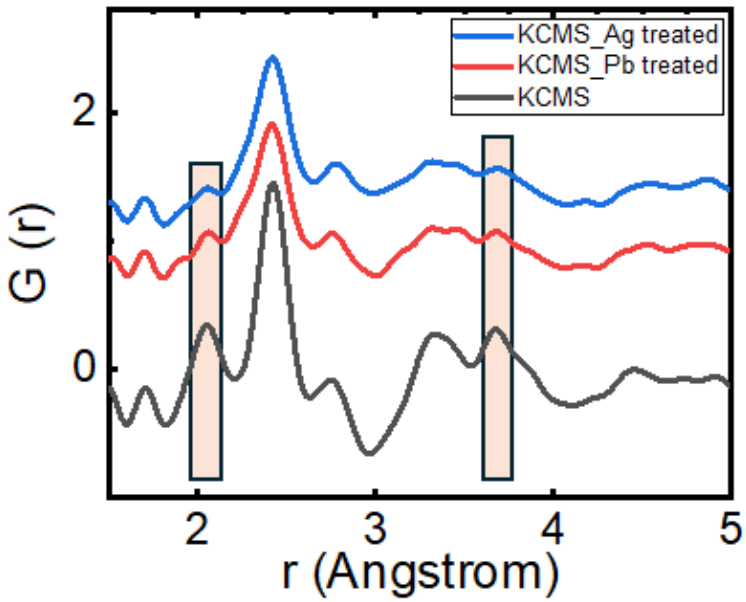



**Figure 4:** A comparison of the pristine and $Ag^{+}$ and $Pb^{2+}$ exposed KCMS showing retention of the local ordering of KCMS gel, light orange shaded lines indicate the change in the intensities between the pristine and $Ag^{+}$ and $Pb^{2+}$ exposed samples.

EDS data of KCMS after an interaction of 100 ppm of $Ag^{+}$, $Pb^{2+}$, or $Hg^{2+}$ ions show the presence of each cation along with a negligible atomic abundance of $K^{+}$ ions (Table S5, S6, S7). These findings are likely to suggest that $K^{+}$ ions of the KCMS are exchangeable with $Ag^{+}$, $Hg^{2+,}$ and $Pb^{2+}$ ions. It is important to note that the ion-exchange phenomenon was reported for other amorphous chalcogels containing electrostatically bound cations. For example, $NH_4^{+}$ of the $(NH_4)_{0.02}MoS_x$[61] was exchanged by $K^{+}$ ions, and $Cs^{+}$ and $Sr^{2+}$ cations exchanged $K^{+}$ ions of K-Sn-Mo-S gels.[26] Apart from this, after the interactions of KCMS with higher concentrations ( ≥1000 ppm) of $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$ the relative atomic abundance of Co decreased by nearly zero percent with the increasing concentration of $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$ (Figure 5, Table S5, S6, S7). For example, after

treating KCMS with 100 and 2000 ppm of $Pb^{2+}$, the residual atomic abundance of Co ion gradually decreases from ~10 % in the pristine KCMS to ~4.4% and 0.2 % of $Co^{2+}$, respectively. A very similar phenomenon was observed for $Ag^{+}$ and $Hg^{2+}$ (Figure 5, Table S5, S6, S7). Overall, our experiments showed a decrease in $Co^{2+}$ ion concentration with the increase of the $Hg^{2+}$, $Ag^{+}$, and $Pb^{2+}$ which may suggest that in addition to $K^{+}$ ions, the $Co^{2+}$ ions of the KCMS are also ions exchangeable.

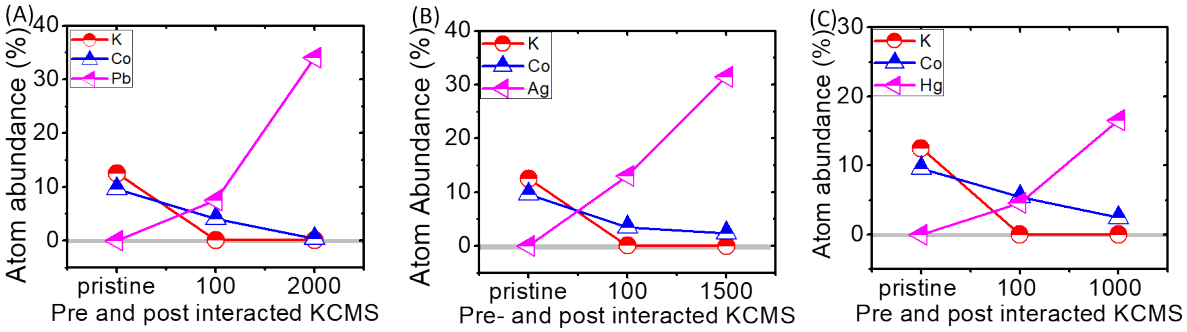



**Figure 5.** The trend in the change of atomic abundance of $K^{+}$ and $Co^{2+}$ ions in KCMS gel with increased concentrations of $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$.

We also investigated the post-interacted solids after treating them with 100 and ≥1000 ppm of $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$ by X-ray Photoelectron Spectroscopy (Figure 6). The XPS of the pristine KCMS shows the presence of a peak centered at 292.1 eV (Figure 6G), which corresponds to K 2p orbital energy.[62] In contrast, the XPS of the 100 ppm $Ag^{+}$, $pb^{2+}$, and $Hg^{2+}$ treated KCMS reveals the absence of a K 2p band but the presence of the bands at 374.0 and 368.0 eV; 104.3 and 100.4 eV; and 143.1 and 138.2 eV (Figure 6 D-F) that correspond to binding energy for $Ag^{+}$ ($3d_{3/2}$; $3d_{5/2}$),[63] $Hg^{2+}$ ($4f_{5/2}$; $4f_{7/2}$)[63,64] and $Pb^{2+}$ ($4f_{5/2}$; $4f_{7/2}$)[63]. The finding suggests the exchange of the $K^{+}$ ions of the KCMS by $Ag^{+}$, $pb^{2+}$, and $Hg^{2+}$ which also corroborates the EDS findings. Moreover, XPS

spectra of the 100 ppm $Ag^+$ sorbed solid KCMS show peaks at ~ 779.4 and 782.0 eV (Figure 6A), corresponding to the main and satellite peaks of $Co^{2+}$ 2p orbitals, respectively. In contrast, these peaks at ~ 779.4 and 782.0 eV were absent at the 1500 ppm $Ag^+$ sorbed KCMS (Figure 6A). Likewise, the Co 2p orbitals peak gradually diminished with an increase in the spiking concentration of $Hg^{2+}$ and $Pb^{2+}$ cations (Figure 6B and C). The above findings imply that polysulfide functional groups have a preferable binding propensity towards softer $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ cations rather than $Co^{2+}$ cations. Furthermore, the intensities of $3d_{3/2}$ and $3d_{5/2}$ orbitals of $Ag^+$, $4f_{5/2}$ and $4f_{7/2}$, orbitals of Hg, and $4f_{5/2}$ and $4f_{7/2}$ orbitals of $Pb^{2+}$ (Figure 6D-F) significantly increase with increasing the spiking concentration of $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ ion.[65] This is because of the incorporation of higher concentrations of $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ in the post-interacted KCMS solids. Hence, EDS and XPS suggest that higher incorporation of $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ is achieved by the exchange of $K^+$ and $Co^{2+}$ ions of the KCMS. This kind of double ion exchange for KCMS is chemically driven by the strong affinity of the soft and polarizable Lewis basic sulfide ions toward the soft Lewis acidic $Ag^+$, $Hg^{2+}$, and $Pb^{2+}$ following the Pearson Hard-Soft Lewis Acid-Base paradigm (HSAB).[27] Hence a concentration-dependent study shows that KCMS undergoes a preferable ion-exchange at first by the exchange of the electrostatically bound $K^+$ ions, and then covalently bound $Co^{2+}$ ions. To the best of our knowledge, KCMS is the first example of the amorphous chalcogel that integrates ion-exchange phenomena in both the ionically and covalently bound cations of the chalcogel matrices.

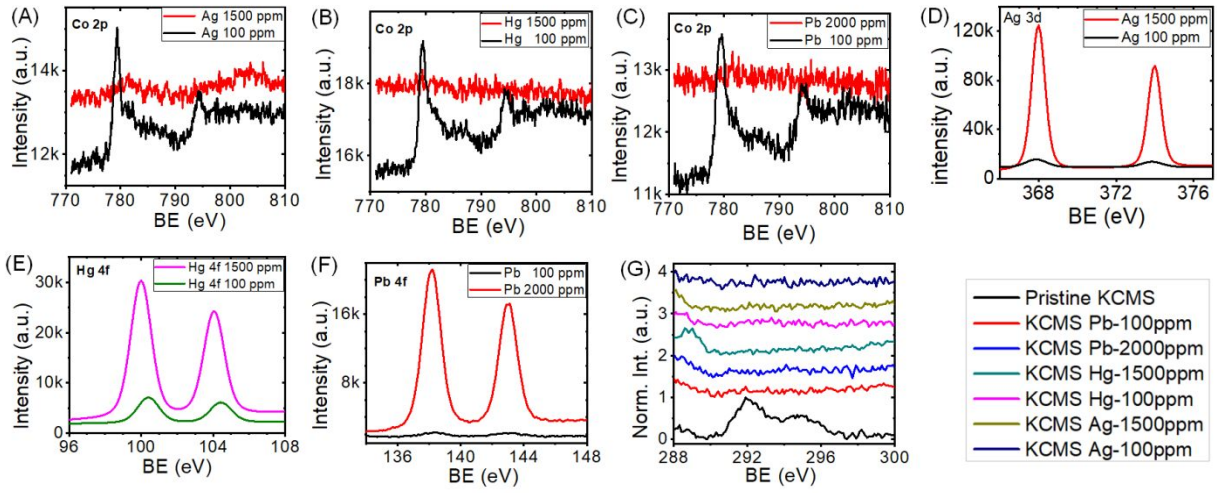



**Figure 6:** XPS spectra of cobalt 2p (A-C); silver 3d (D); mercury 4f (E); and lead 4f (F); potassium 2p (G) orbitals after interaction of KCMS gels with different concentrations of $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$.

It is important to note that the dissolution of cobalt ions from sorbent material can make it unlikely for drinking or household water treatment but could be useful for industrial wastewater treatment of highly toxic $Pb^{2+}$, $Hg^{2+}$, and $Ag^{+}$ for recycling purposes, non-household applications or discharging them into natural water bodies. Apart from this decontamination of $Co^{2+}$ from the KCMS-treated wastewater can be done by the coprecipitation method as the second treatment method. However, this work introduces KCMS as multi-ion exchangeable materials that can exchange both covalently and ionically cations following the Hard-Soft Lewis Acid-Base principles. This finding can potentially open opportunities for designing and synthesizing highly efficient and high-capacity chalcogel-based sorbent using eco-friendly transition metals for cobalt.

## CONCLUSIONS

The KCMS chalcogel was synthesized in solution at room temperature. The highly disordered

incoherent structural features of KCMS chalcogels were evidenced by X-ray powder diffraction and Pair Distribution Function (PDF). The KCMS xerogel is highly efficient in removing chemically toxic heavy metal ions, particularly $Ag^{+}$, $Hg^{2+}$, and $Pb^{2+}$, achieving over 99.9% removal with a distribution coefficient as high as $\geq 10^{8}$ mL/g in just half an hour in deionized water solutions. Moreover, $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$ exhibit exceptionally high sorption capacities of 1377, 1146, and 460 mg/g, respectively. Furthermore, we found that this material is exceptionally efficient in removing $Ag^{+}$, $Pb^{2+}$, and $Hg^{2+}$ from highly contaminated water. For instance, it removes over 99% $Ag^{+}$ and $Pb^{2+}$ with a $K_d$ of $10^{5}$ mL/g from the Mississippi River which contains over 10,000 ppb of each cation. The selectivity order observed was $Pb^{2+} > Ag^{+} > Hg^{2+} > Cu^{2+} >> Cd^{2+} > Ni^{2+}$. The remarkable efficiency of KCMS in separating $Pb^{2+}$ and $Ag^{+}$ is likely due to the unprecedented and selective ion exchanges of electrostatically bound $K^{+}$ and covalently bound $Co^{2+}$ cations and surface sorption. The chemically soft polarizable Lewis basic (poly)sulfide functional groups KCMS offer binding propensities through covalent binding toward Lewis acidic metal cations and the degree of their binding propensity is governed by Pearson's Hard-Soft Lewis Acid-Base (HSAB) paradigm.[27] Despite its irreversible sorption properties, KCMS stands out due to its exceptional sorption capacity, fast sorption kinetics, high removal efficiency to trace levels, scalability, solution processability at room temperature, and unique sorption mechanisms, making it an ideal sorbent for chemically soft Lewis acidic heavy metal cations in aqueous solutions. Overall, this study reveals the immense potential of chalcogels for the removal of toxic heavy metal ions and introduces a new paradigm in the design principles of multi-ion-exchangeable chalcogels.

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## Data availability

Data for this article, including material Characterization, heavy metal removal performance sorption kinetics, and capacity are available at S. M. Islam, email: Muhammad.s.islam@jsums.edu

## Author Contributions

This manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

## Conflict of Interest

The authors declare no conflict of interest

## Supporting Information

The supporting information file is available: Synthesis and characterization of pristine and post-

sorption KCMS gel by XRD, Raman, EDS, and TEM analysis. Details on uptake study as well as sorption kinetics and capacity of heavy metal analysis by ICP-MS.

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**Data availability Statement**

Data for this article, entitled "Ion Exchangeable K-Co-Mo-$S_x$ Chalcogel ─ High Capacity Removal of $Pb^{2+}$ and $Ag^{+}$ and their Underlying Mechanisms" including material Characterization, heavy metal removal performance sorption kinetics, and capacity have been included as part of the Supplementary Information and others data are available at S. M. Islam, email: Muhammad.s.islam@jsums.edu.

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