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Super-selective Removal of Lead from Water by Two-Dimensional MoS₂ Nanosheets and Layer-stacked Membranes

Research article

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23 Abstract

24 Point-of-use (POU) devices with satisfactory lead (Pb^{2+}) removal performance are urgently
25 needed in response to recent outbreaks of lead contamination in drinking water. This study
26 experimentally demonstrated the excellent lead removal capability of two-dimensional (2D)
27 MoS_2 nanosheets in aqueous form and as part of a layer-stacked membrane. Among all materials
28 ever reported in the literature, MoS_2 nanosheets exhibit the highest adsorption capacity (740
29 mg/g), and the strongest selectivity/affinity towards Pb^{2+} with a distribution coefficient K_d that is
30 orders of magnitude higher than that of other lead adsorption materials (5.2×10^7 mL/g). Density
31 functional theory (DFT) simulation was performed to complement experimental measurements
32 and to help understand the adsorption mechanisms. The results confirmed that the cation
33 selectivity of MoS_2 follows the order $\text{Pb}^{2+} > \text{Cu}^{2+} \gg \text{Cd}^{2+} > \text{Zn}^{2+}$, $\text{Ni}^{2+} > \text{Mg}^{2+}$, K^+ , Ca^{2+} . The
34 membrane formed with layer-stacked MoS_2 nanosheets exhibited a high water flux (145 L/
35 $\text{m}^2/\text{h}/\text{bar}$), while effectively decreasing Pb^{2+} concentration in drinking water from a few mg/L to
36 less than 10 $\mu\text{g}/\text{L}$. The removal capacity of the MoS_2 membrane is a few orders of magnitude
37 higher than that of other literature-reported membrane filters. Therefore, the layer-stacked MoS_2
38 membrane has great potential for POU removal of lead from drinking water.

39

40 KEYWORDS: layer-stacked MoS_2 membrane; point-of-use device; lead contamination; drinking
41 water; super-selective adsorption; high adsorption capacity

42

43 **Table of Contents (TOC)**

44

INTRODUCTION

Toxic heavy metal contamination of freshwater and drinking water has become a critical challenge for human society. Particularly, lead (Pb^{2+}) has been recognized as one of the most toxic metals worldwide and there have been cases of lead contamination of tap water in various cities (e.g., Washington, DC; Flint, MI; and Newark, NJ) in the United States. A major source of lead in drinking water is the lead-containing plumbing in water distribution systems like pipes, solders, and fittings. As aged lead-containing pipelines are still used, lead concentrations can be on the order of tens of milligrams per liter in the aftermath of man-made mismanagement or natural disasters.^{1,2} This is several orders of magnitude higher than the U.S. EPA lead action level (15 $\mu\text{g/L}$) and the WHO guideline value (10 $\mu\text{g/L}$).^{3,4} Long-term exposure to lead, even at extremely low concentrations, increases the blood lead level due to its bio-accumulative nature, causing severe adverse health effects in the nervous system and brain, particularly in infants and children.⁵

To remove lead from drinking water, especially for daily-use in rural areas or for responding to emergency lead contamination incidents, portable point-of-use (POU) adsorption technologies are essential because of their flexibility, ease of operation, and cost effectiveness. Some promising adsorbents targeting heavy metal remediation have been recently identified, including metal–organic frameworks (MOFs),^{6, 7} graphene-based materials,⁸ covalent organic frameworks,^{9, 10} layered nanomaterials¹¹⁻¹⁴, and natural materials like biochar¹⁵. However, sorption materials that have ultrahigh affinity and selectivity to lead are still lacking. High selectivity is extremely important because one challenge hindering effective removal of lead from drinking water is the presence of interfering species. In addition, the adsorption materials used in POU applications should possess attributes such as high porosity, adsorption-site accessibility, and

homogeneous binding sites to achieve fast kinetics and high capacity.

Two-dimensional (2D) molybdenum disulfide (MoS_2), one of the most widely researched transition metal dichalcogenides (TMDs), is an ideal adsorbent material for heavy metal remediation because of its large surface area, and is abundant active sulfur sites that have a high affinity to heavy metals.^{16, 17} Although MoS_2 is a naturally occurring mineral, the direct use of bulk MoS_2 in heavy metal remediation is impossible because the interlayer spacing (0.63 nm) is so small that targeted heavy metal ions are unable to access the interior sulfur atoms. Synthetic 2D MoS_2 nanomaterials (*e.g.*, flower-like aggregates) have been explored as adsorbents for toxic transition metal (Hg^{2+} , Pb^{2+} , Ag^+ , Zn^{2+} , Cd^{2+}) remediation, showing moderate-to-high adsorption capacities¹⁸⁻²⁵. However, little investigation has been done to quantify the affinity and selectivity of MoS_2 -based adsorbents.²⁶ The surface area of MoS_2 available for adsorption is also compromised due to the aggregation of MoS_2 nanosheets during hydrothermal synthesis. In contrast, the exfoliated MoS_2 monolayers possess the highest theoretical surface area. However, limited work has been done investigating its application as an adsorbent in a POU device for lead ion removal.

To address the above research needs, we systematically studied the adsorption of Pb^{2+} by MoS_2 monolayers and the effects of interfering ions and compared its selectivity and capacity to that of other heavy metal ions. Batch tests and DFT simulations were used to unveil the selectivity and adsorption mechanisms of MoS_2 towards various ions. The layer-stacked MoS_2 structure with confined and ordered nanochannels was employed as a POU filter, and its performance and mechanism for removing Pb in continuous filtration was investigated to reveal the potential in practical applications.

MATERIALS AND METHODS

MoS₂ monolayer and membrane preparation. To prepare chemically exfoliated monolayer MoS₂ nanosheets,²⁷ 5 ml of 1.6 M n-butyllithium in hexane solution was added to ~500 mg of bulk MoS₂ powder (~ 2 μ m, Sigma-Aldrich), and the mixture was kept at room temperature for 2 d in a nitrogen-filled glovebox with mild stirring. The resulting lithium-intercalated product was rinsed with hexane to remove organic reactants and by-products. The purified intercalated product was immediately exfoliated by reaction with DI water in an ultrasonic bath for 1 h. MoS₂ nanosheets well-dispersed in solution were obtained after dialysis of the dispersion against DI water to remove inorganic byproduct LiOH. The total MoS₂ concentration was determined through digestion in 0.2 M HNO₃ and 0.5 M H₂O₂ solution, followed by measurement of the soluble Mo species concentration in ICP-OES (Agilent 720, Agilent Technologies, Santa Clara, CA). Dispersions of chemically exfoliated MoS₂ samples were stored in 4 °C for further use. To prepare layer-stacked MoS₂ membranes, a dispersion containing 4 mg MoS₂ was filtered through a polyethersulfone (PES) ultrafiltration membrane with a nominal pore size of 30 nm (Sterlitech, Kent, WA), generating an MoS₂ membrane with a thickness of ~ 600 nm.

Metal ion adsorption by suspended MoS₂ nanosheets. Metal cation adsorption by MoS₂ nanosheets was studied in batch experiments. The metal cations tested include Mg²⁺, K⁺, Ca²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Cu²⁺ and Pb²⁺ in their nitrate salt forms. After mixing MoS₂ nanosheets (100 mg/L) with individual cations (~ 5 mg/L) in 10 mL buffer solutions (MES, 10 mM, pH 6) for 1 d, cation-adsorbed nanosheets were removed through 0.22 μ m PES syringe filters (VWR), and the cation concentrations in the filtrate solutions were determined using ICP-OES or ICP-MS (Agilent 7700 Series) for low concentration (≤ 10 μ g/L). The removal is calculated as $R = 100 \times$

112 $(C_0 - C_f)/C_0$ %, where C_0 and C_f are the initial and final cation concentrations (mg/L),
113 respectively. The distribution coefficient is calculated as $K_d = (V[(C_0 - C_f)/C_f])/m$, where V is the
114 solution volume (mL), and m is the adsorbent mass (g).

115 To characterize the competitive adsorption of metal cations, batch experiments were
116 carried out with a mixed solution containing ~5 mg/L of each cation (Mg^{2+} , K^+ , Ca^{2+} , Ni^{2+} , Cd^{2+} ,
117 Zn^{2+} , Cu^{2+} and Pb^{2+}) and 100 mg/L MoS_2 nanosheets. A solution mimicking tap water
118 composition was prepared by spiking DI water with NaCl (280 mg/L), $CaCl_2$ (150 mg/L) and
119 $MgSO_4$ (75 mg/L). Batch tests were also used to understand the Pb^{2+} removal capacity, kinetics,
120 and selectivity.

121 In order to test the regeneration capability of MoS_2 , we used a strong chelating agent
122 EDTA, which has a Pb -EDTA²⁻ formation constant of approximately 10^{18} to recover Pb from
123 MoS_2 . In each repeated test, 50 mg/L Pb^{2+} and 100 mg/L MoS_2 was added to 40 mL of pH 6
124 buffer solution, and the sample was then mixed for 2 h before the solid Pb - MoS_2 was collected by
125 vacuum-filtration onto a PES membrane. To recover the MoS_2 , 40 mL of 5 mM EDTA solution
126 was added to the collected Pb - MoS_2 to allow the release of Pb from MoS_2 for 2 h, then the
127 regenerated MoS_2 was recollected by vacuum filtration for use in the next cycle.

128 **Pb removal by layer-stacked MoS_2 membranes.** The filtration experiments were performed
129 using a dead-end stirred cell filtration system (Model 8050, EMD Millipore) with a total internal
130 volume of 50 mL and an active surface area of 13 cm². The solution in the chamber was
131 continuously mixed with a suspended magnetic stirrer at 200 rpm. The chamber was filled with
132 aqueous solution containing Pb^{2+} at various concentrations (0.25, 1, 3 mg/L), which was
133 continuously supplied from a stock solution in a plastic container. The filtration experiments

134 were started by applying ~ 10 psi pressure to the chamber by means of compressed N₂. Ten-mL
135 samples of the filtrate were periodically collected and analyzed by ICP-MS.

136 **Density functional theory (DFT) simulations.** All simulation results were calculated using DFT
137 software VASP.²⁸ The exchange-correlation functional was described using generalized gradient
138 approximation (GGA) with Perdew-Burke-Ernzerhof (PBE),²⁹ and the ion-electron interaction
139 was treated with the projector augmented wave (PAW) method.³⁰ The cutoff energy was 520 eV
140 and the energy convergence criterion was 10⁻⁵ eV/cell. The conjugate gradient method was
141 adopted for the geometry optimization. The Brillouin zone was represented by a
142 Monkhorst–Pack special k-point mesh³¹ of different sizes depending on the MoS₂ size. For all
143 calculations, the van der Waals (vdW) interaction was included using a dispersion correction term
144 from the DFT-D3 method.³² A large vacuum space of 30 Å was used to avoid any interaction of
145 the MoS₂ sheets with their images. The electron localization function (ELF) calculation was also
146 performed for detailed data analysis.³³ ELF is derived from the calculation of Pauli repulsion with
147 values normalized between 0 and 1.³⁴ Notably, the Hubbard U correction was not added here
148 since little changes were found for the electronic structure of MoS₂ in previous studies.³⁵⁻³⁸

149 **Material and membrane characterization.** MoS₂ nanosheets were characterized through
150 transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray
151 photoelectron spectroscopy (XPS). TEM images were obtained with a JEM-2100F. The AFM
152 images were obtained in air using a Bruker Dimension Icon in tapping mode. The XPS
153 measurement was conducted with a K-Alpha XPS spectrometer (Thermo Scientific Ltd, East
154 Grinstead, UK). The zeta potential measurement was performed on a Zetasizer Nano-ZSP
155 analyzer (Malvern, Westborough, MA). Cross-sectional images of a layer-stacked MoS₂ were

recorded by a field emission SEM (Zeiss Gemini Ultra-55, Jena, Germany).

RESULTS AND DISCUSSION

Synthesis of MoS₂ nanosheets and layer-stacked membranes. We prepared MoS₂ monolayer nanosheets from MoS₂ bulk material through chemical exfoliation,^{27, 39} engineered them into layer-stacked membranes, and tested the Pb removal by both configurations of MoS₂ (Figure 1a-c). The as-prepared MoS₂ nanosheets were highly dispersible in water because of their uniformly distributed negative charge on the surface (*e.g.*, each MoS₂ unit cell is believed to carry -0.25 eV),⁴⁰ as confirmed by a zeta potential of -40 to -50 mV in a wide pH range (Figure S1a). According to the TEM (Figure S1b) and AFM (Figure 1d) images, a majority of the exfoliated MoS₂ nanosheets had a lateral dimension of 100 to 500 nm and a monolayer thickness of ~1.1 nm. The phase composition of MoS₂ nanosheets characterized by XPS (Figure S1c-d) consisted of 40% 2H-MoS₂ and 60% 1T-MoS₂, which is consistent with the results of exfoliation-induced phase transformation reported previously.³⁹ Layer-stacked MoS₂ membranes were fabricated by filtration leading to a stable interlayer spacing of ~ 1.2 nm, which was naturally formed and stabilized by a balance between attractive van der Waals and repulsive hydration forces according to our previous study.⁴¹ In this stacked configuration, MoS₂ membranes maintain an ultrahigh surface area, exposing all sulfur atoms on each nanosheet as accessible metal-binding sites, and thus potentially enabling a POU device with continuous water flow as well as high metal adsorption capacity.

Figure 1. Schematic illustration of exfoliating bulk MoS₂ materials (a) to create an aqueous suspension of MoS₂ monolayer nanosheets (b) and reassembling the nanosheets into a layer-stacked MoS₂ membrane (c) for adsorptive filtration targeting the removal of toxic ions. (d) The AFM image of a monolayer MoS₂ nanosheet with a depth profile revealing a thickness of ~ 1.1 nm.

Selectivity of MoS₂ nanosheets towards different cations. To determine the selectivity of MoS₂ towards different cations, we first evaluated the adsorption of several toxic transition metal cations (Ni²⁺, Cd²⁺, Zn²⁺, Cu²⁺ and Pb²⁺) and some common background cations (Mg²⁺, K⁺, Ca²⁺) by MoS₂ monolayers in batch experiments (see details in Table S1 and S2). Figure 2a (blue hatched bars) shows the calculated removal of various cations in individual ion tests. MoS₂ nanosheets demonstrated nearly complete removal of Pb²⁺ and Cu²⁺ by effectively decreasing their concentrations from 5 mg/L, to 4 and 1 μg/L respectively. In comparison, the removal efficiency was relatively high (~ 90%) for Cd²⁺, moderate (30 to 50%) for Zn²⁺, Ni²⁺ and Ca²⁺, and very low (< 20%) for Mg²⁺ and K⁺. In addition, the high affinity of MoS₂ nanosheets towards Pb²⁺ can be demonstrated by a low threshold concentration (0.1 mM) that induces visible aggregation of

MoS₂ nanosheets within half an hour. While for poorly adsorbed ions (e.g., Mg²⁺), a higher threshold concentration for aggregation (0.5 mM) was observed (Figure S2).⁴²

To directly compare the affinity of MoS₂ nanosheets towards different cations in a competitive environment, we also conducted the adsorption experiments in an ion mixture containing all eight cations of the same concentration (~ 5 mg/L). As shown in Figure 2a (red unhatched bars), MoS₂ nanosheets maintained excellent removal of Pb²⁺ and Cu²⁺ by decreasing their concentrations from ~ 5 mg/L to a few micrograms per liter, which was in good agreement with those observed in individual ion tests. However, the removal of each of the other cation species was much lower than that when tested individually, indicating that the preferred adsorption of Cu²⁺ and Pb²⁺ significantly decreased the available sorption sites for other ions.

Figure 2. Characterization of the selectivity and capacity of Pb²⁺ adsorption by suspended MoS₂ nanosheets. (a) Removal of various cations by MoS₂ nanosheets in individual ion solutions and in a mixture containing all ions of equal concentration (5 mg/L). (b) Distribution coefficients K_d of various cation species. (c) Pb²⁺ removal by MoS₂ in the presence of Na⁺, Ca²⁺ or tap water impurities. The dashed line represents the maximum removal capacity observed in the pure water baseline experiment. (d) Isotherm of Pb²⁺ adsorption by MoS₂ fitted by Langmuir model (dash line). (e) Kinetics of Pb²⁺ adsorption

at various initial Pb^{2+} concentrations. (f) Comparison of the adsorption capacity ($q_{\max}$) and distribution coefficient (K_d) of MoS_2 nanosheets with those of other benchmark materials reported in the literature.^{6, 11, 43-55}

The affinity of MoS_2 nanosheets to various cations can be compared by calculating their distribution coefficients K_d (Figure 2b). According to the individual cation test results, the K_d values of MoS_2 nanosheets for Pb^{2+} and Cu^{2+} are both $>10^7$ mL/g, which are 2 to 4 orders of magnitude higher than those for other metal cations, revealing the excellent adsorptive selectivity of MoS_2 nanosheets towards Pb^{2+} and Cu^{2+} . To further reveal the relative affinity of MoS_2 nanosheets to Pb^{2+} and Cu^{2+} , we conducted competitive tests where the initial concentrations of Cu^{2+} and Pb^{2+} remained constant at ~ 5 mg/L, but the initial concentrations of MoS_2 nanosheets were reduced from 100 mg/L to 30, 15, and 5 mg/L, respectively. As shown in Figure S3 and Table S3, at lower concentrations (30 and 15 mg/L) of MoS_2 nanosheets, Pb^{2+} removal was still close to 100%, while the removal of Cu^{2+} decreased from 100% to 91.2% and 36.1% respectively. These results indicate that when MoS_2 was limited in quantity, its adsorption sites highly preferred Pb^{2+} over Cu^{2+} . Only when the concentration of MoS_2 further decreased to 5 mg/L was there a slight decline in Pb^{2+} removal, whereas Cu^{2+} removal was very low (6.1%).

Overall, the MoS_2 monolayer displayed an adsorption affinity in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$, $\text{Ni}^{2+} > \text{Mg}^{2+}$, K^+ , Ca^{2+} (Figure 2b). This is consistent with the hard-soft principle in Lewis acid-base theory, i.e., the sulfur sites on MoS_2 offer strong soft-soft interactions towards soft acids (metal ions such as Pb^{2+} , Cu^{2+} , and Cd^{2+}). The high affinity/selectivity towards Pb^{2+} over hard acid species (Mg^{2+} , K^+ , Ca^{2+}) reveals the great promise of using MoS_2 nanosheets in the development of household POU devices for the removal of lead from drinking water. In addition, we tested the interference of Pb^{2+} adsorption by high concentrations of common cations (e.g., Na^+

and Ca^{2+}) that are ubiquitous in drinking water. We found that the presence of a high concentration of these background ions (up to 1 M NaNO_3 , 1 M $\text{Ca}(\text{NO}_3)_2$, or concentrations characteristic of a tap water mimic, with detailed composition data in the Supporting Information) did not affect Pb^{2+} removal by MoS_2 (Figure 2c).

The Pb^{2+} adsorption capacity and kinetics were further studied to elucidate the removal mechanism. The adsorption of Pb^{2+} onto MoS_2 monolayers was examined by varying the initial Pb^{2+} concentration in the range of 25 to 150 mg/L. As shown in Figure 2d, the adsorption isotherm data can be better fitted by the Langmuir model than the Freundlich model (Figure S4), indicating the adsorption of a monolayer Pb^{2+} onto the MoS_2 nanosheet surface. According to the model, MoS_2 nanosheets have a maximum adsorption capacity of 740 mg/g toward Pb^{2+} (Figure 2d and Figure S5). The Pb^{2+} removal also depends on pH conditions (Figure S6). Higher removal capacity is found at neutral pH (~ 740 mg/g) than at acidic conditions (e.g., ~ 350 mg/g at pH 3). The decrease in Pb^{2+} adsorption at lower pH indicates that the Pb^{2+} captured by MoS_2 may be attributed to the ion exchange with protons on the nanosheets ($\text{H}_{0.25}\text{MoS}_2$),⁴⁰ the deprotonation of which is inhibited by low pH. Similar Pb^{2+} adsorption mechanisms and pH effects have been observed with other functional materials.^{43, 55} In this study, pH 6 was adopted to investigate the fundamental interactions between MoS_2 and Pb^{2+} in order to avoid the interference of possible hydroxide precipitate at alkaline conditions. Fast removal kinetics (2-3 logs Pb^{2+} removal within 2 min, as shown in Figure 2e) was observed regardless of initial Pb^{2+} concentration in solution (0.25 to 20 mg/L). The regeneration of MoS_2 can be achieved by using strong chelating agents with a formation constant higher than $10^{11.4}$ (Figure S7). In our study, EDTA with a formation constant of 10^{18} was chosen for regeneration. The regeneration of MoS_2 could maintain a 85-95% lead removal in 2 to 5 repeated regeneration cycles (Figure S8). The slight reduction in removal

efficiency during regeneration was likely caused by the aggregation or partial oxidation of MoS₂ nanosheets.

Overall, the MoS₂ nanosheets studied in this work have superior lead adsorption capabilities compared with other materials reported so far. As shown in Figure 2f, our exfoliated MoS₂ nanosheets demonstrate a high Pb²⁺ adsorption capacity (740 mg/g) and an extremely high affinity K_d ($5.2 \pm 1.9 \times 10^7$ mL/g), outperforming previously reported materials including MOFs, layered metal sulfides, and sulfur-functionalized nanomaterials.^{6, 11, 43-49} Note that adsorbents with K_d values in the order of magnitude of 10^4 are considered to have outstanding selectivity.⁵⁶ Examples include sulfur-based sorbents such as S_x- and MoS₄²⁻-intercalated LDH (10^3 to 2.6×10^5 mL/g),^{11, 46} layered metal sulfides (5.4×10^5 to 2.1×10^6 mL/g),^{43, 47, 49} MoS₂ hydrogel (1.32×10^4 mL/g),⁵⁰ and others (10^3 - 10^5 mL/g).⁵³⁻⁵⁵ More details can be found in Table S4. The MoS₂ nanosheets indeed exhibit the highest K_d (10^7 mL/g) among all materials to the best of our knowledge, demonstrating their excellent selectivity toward Pb²⁺.

Investigation of adsorption mechanism. To further elucidate the adsorption mechanisms, we used DFT simulation based on first-principle calculations to study the interactions between metal ions and 2H-MoS₂. 2H-MoS₂ was chosen for modelling because of its thermodynamic stability and common presence in nature. As MoS₂ nanosheets are partially reduced during the intercalation/exfoliation process, they are negatively charged and have a formula of H_{0.25}MoS₂ or MoS₂^{-0.25}.⁴⁰ According to this formula, we built a 4×4 MoS₂ supercell with 4 hydrogen atoms evenly distributed on the surface (H₄(MoS₂)₁₆, Figure S14). Since all reactions take place in aqueous solution, the ions are present in the hydrated form, and the number of water molecules in the hydration shell is determined based on literature data.⁵⁷ Therefore, the adsorption of a divalent

279 metal ion (M^{2+}) onto MoS_2 can be described in equation 1.

281 where n varies in the range of 1 to 24 depending on the Pb/S coverage ratio ranging from 1/32 to
 282 3/4. Accordingly, the corresponding free energy of adsorption ($\Delta G_{f,ads}$) is calculated by the
 283 following equation:

$$284 \quad \Delta G_{f,ads} = E_{[M_n(MoS_2)_{16}]^{2n-4}} + 4E_{(H_2O)_2H^+} + (n-2)E_{(H_2O)_4} - E_{H_4(MoS_2)_{16}} - nE_{(H_2O)_4M^{2+}} \quad (2)$$

285 where E represents the internal energy of the corresponding compound, which can be obtained
 286 from the first-principle DFT calculations. A detailed illustration of the adsorption reaction and
 287 the methodology used to calculate the free energy is discussed in the Supporting Information. A
 288 negative free energy $\Delta G_{f,ads}$ indicates that the adsorption is energetically favorable, and vice versa.

289

Figure 3. Mechanistic investigation of lead adsorption by DFT simulation and XPS spectra. The top-down and cross-sectional views of the electron localization function (ELF, with detailed explanation in Supporting Information) for the Pb-MoS₂ double bond formed on a bridge S-S site (a) and a single bond formed on a top-S site (b). (c) XPS spectra of Pb peaks with the Pb/S coverage ratio increasing from 1/32 to 5/32, which correspond to the MoS₂-Pb mass ratio ranging from 10 to 2.5 (see SI for calculation process). The peaks at higher (red) and lower (blue) binding energies are most likely attributed to single bonds on the top-S and double bonds on the bridge S-S sites, respectively. (d) The free energy of Pb²⁺ adsorption on MoS₂ surface as a function of Pb/S coverage ratio. (e) The maximum bond energy for the binding between cations and MoS₂.

The binding mechanisms between Pb²⁺ and MoS₂ nanosheets are affected by the Pb/S coverage ratio. The most stable (energetically favorable) binding site on MoS₂ is the Bridge S-S site (Figure 3a), where a Pb²⁺ binds to two neighboring S-atoms with an equal bond length of ~ 2.7 Å. However, when the Pb/S coverage ratio increases, the dominating binding site shifts to the

304 Top-S site, where a Pb^{2+} binds to only one S atom with a bond length of $\sim 2.5 \text{ \AA}$ (Figure 3b). The
305 Pb-MoS₂ double bond formed at the Bridge S-S position (binding energy of -1.3 eV) is stronger
306 than the single bond at the Top-S position (binding energy of -1.0 eV). A more detailed
307 description of the binding mechanism, formation energy, bond length, geometry, and effects of
308 Pb-S coverage can be found in Tables S5 and S6, Figures S19 to S22. The simulation results are
309 correlated with the deconvolution of Pb 4f peaks in the XPS spectra at different Pb/S coverage
310 ratios. As shown in Figure 3c, when the Pb/S coverage ratio increases from 1/32 to 5/32 (i.e., the
311 MoS₂/Pb mass ratio decreases from 10 to 2.5), the component peak at higher binding energy (red
312 line) increases in strength, corresponding to more single bonds on Top-S sites, while the
313 component peak at lower binding energy (blue line) becomes weaker, corresponding to less
314 double bonds on the Bridge-S-S sites. The XPS results are consistent with the simulation results.

315 The overall free energy ($\Delta G_{\text{f,ads}}$) for Pb adsorption onto MoS₂ is strongly affected by the
316 Pb/S coverage (Figure 3d). The free energy of adsorption increases with increasing Pb/S coverage
317 ratio, indicating that the adsorption of Pb becomes weaker when more Pb is adsorbed onto MoS₂
318 surfaces. The free energy becomes positive when Pb/S coverage is over 0.31, demonstrating that
319 the adsorption of more Pb beyond the 31% coverage is energetically unfavorable. The 31%
320 coverage amounts to an adsorption capacity of 802 mg/g, which is very close to our experimental
321 results (740 mg/g).

322 To understand the stronger selectivity towards Pb^{2+} than towards other cations, the binding
323 energy for other cations were also calculated using the DFT model. The favorable binding
324 mechanism for each metal species is shown in Table S7. It was found that for almost all divalent
325 cations except Ca^{2+} , the most stable (energetically favorable) binding mechanism is the double

bond formed at Bridge S-S sites. The binding of Ca^{2+} is unique because the bonds on all binding sites exhibit a positive formation energy, indicating unfavorable adsorption. The formation energy of the most favorable binding of each cation on the MoS_2 nanosheet is correlated with the experimentally measured K_d values in Figure 3e. In general, a negative formation energy of around -1 eV (for Pb^{2+} , Cd^{2+} , and Cu^{2+}) corresponds to a high K_d value (above 10^5 mL/g), demonstrating good consistency between simulation and experimental results. Among all metal ions analyzed, the formation energy of Pb- MoS_2 has the most negative value (-1.3 eV), indicating stronger bonding and more facile interactions of Pb^{2+} than those of Cu^{2+} and Cd^{2+} with MoS_2 nanosheets, consistent with its highest K_d value measured experimentally. The formation energy of Zn^{2+} , Mg^{2+} and Ca^{2+} is much less negative or becomes positive (> -0.4 eV), consistent with their low K_d values (below 10^4 mL/g) measured experimentally. It's worth noting that the interactions between MoS_2 and representative ions were simulated exclusively with 2H- MoS_2 , and the potential effects of various MoS_2 phases on the adsorption efficiency should be investigated via experimental tests and theoretical simulations in the future studies.

Besides adsorption, metal ion removals can be potentially caused by redox reactions and/or precipitation formation with MoS_2 nanosheets or soluble molybdate species. To explore if these mechanisms are present in removing Pb^{2+} and other metal ions tested here, we carried out extensive XPS characterization of the metal-adsorbed MoS_2 samples (Pb-, Cu-, Cd-, Ni-, Zn- MoS_2). As shown in Figure S9a, compared to the pristine MoS_2 , all metal-adsorbed MoS_2 samples exhibit similar Mo and S peak positions and intensities. Meanwhile, the absence of oxidized S at 168 eV and constant 1T/2H ratios indicate no direct redox reaction occurring between MoS_2 and metal species tested here (Figure S9b and S9c). This is consistent with the previous findings that MoS_2 can not reduce Pb^{2+} or Cu^{2+} , although redox reaction contributes

greatly to the removal of Ag^+ and Hg^{2+} that leads to oxidized S and reduced 1T/2H ratios.²⁶ We observed weak peaks of molybdate, which often co-exists in the MoS_2 suspension due to slow oxidative dissolution of MoS_2 by ambient oxygen. Based on the XPS characterization (Figure S9b), even if we assume all the molybdate contributes to Pb removal by forming precipitates, the precipitation accounts for less than ~10 % of the total Pb removal (see Supporting Information for calculation).

Layer-stacked MoS_2 as POU filter. Excellent capacity and selectivity are the pre-requisites for MoS_2 monolayers as potential building blocks for a POU filter. With these aspects demonstrated above, we further used MoS_2 monolayers to synthesize a layer-stacked MoS_2 membrane, and explored its potential for POU removal of lead from drinking water. The MoS_2 membranes were tested in filtration experiments with feed water containing various concentrations of Pb^{2+} . The membrane maintained a constant water flux ($145 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) due to stable 2D nanochannels formed between stacked MoS_2 nanosheets with an interlayer distance of 1.2 nm (Figure S10). The interlayer spacing is large enough to allow Pb^{2+} to enter the 2D nanochannels in the MoS_2 membrane and adsorb it onto the channel walls. As a result, Pb^{2+} concentration is efficiently lowered from 0.25-3 mg/L in the feed water, to less than 10 $\mu\text{g/L}$ in the effluent, which is the WHO guideline value. Since the MoS_2 membrane mainly removes Pb^{2+} by adsorption, there would be a breakthrough point when the effluent concentration rises above 10 $\mu\text{g/L}$. The total effluent volume at the breakthrough point defines the treatment capacity of the adsorptive membrane. As shown in Figure 4a, when the Pb^{2+} concentration in feed water was 0.25, 1, and 3 mg/L, the treatment capacity of the MoS_2 membrane was 800, 180, and 70 mL, respectively. It is

371 estimated that the residence time of Pb^{2+} in the MoS_2 membrane is merely 0.02 s (see calculation
 372 in Figure S10), so the breakthrough is most likely controlled by a dynamic process instead of
 373 reaching an equilibrium condition for adsorption. Therefore, the treatment capacity of MoS_2
 374 membranes can be further improved by increasing the residence time, e.g., by synthesizing a
 375 thicker membrane (Figure S12).

377 **Figure 4.** Layer-stacked MoS_2 membrane as a POU filter. (a) The performance of MoS_2 membranes in
 378 filtering a feed water containing 0.25 to 3 mg/L Pb^{2+} . The treatment capacity is defined as the total
 379 effluent volume at the breakthrough point, which was reached when the effluent Pb^{2+} concentration
 380 reached 10 $\mu\text{g/L}$. The cross-sectional SEM (b) and XPS depth profile (c) of the MoS_2 membrane after
 381 filtering Pb^{2+} water (see Figure S11 for detailed peak intensity evolution). (d) The regeneration of MoS_2
 382 membrane using EDTA cleaning. (e) Treatment capacities (L-water/g-material) of MoS_2 membranes and
 383 other adsorptive membranes reported in the literature. Membranes fabricated by commercial materials are
 384 represented by red hollow symbols, and those by lab-synthetic materials are represented by amber filled
 385 symbols.

386 SEM and XPS were used to characterize a used MoS_2 membrane after being tested with
 387 1 mg/L Pb^{2+} feed solution and reaching the breakthrough point in filtration. The MoS_2 membrane

maintains a stacked structure as shown in the cross-sectional SEM image (Figure 4b). The distribution of adsorbed lead in the MoS₂ membrane can be observed in the depth profile of the S 2p and Pb 4f peaks obtained by etching 300 nm (15 times × 20 nm etching depth) into the MoS₂ membrane during XPS characterization (Figure 4c). The Pb/S atomic ratio is high (12 %) on the membrane surface, and gradually decreases to around 5 % at 100 nm depth and below. The higher Pb content on the membrane top surface could be partially attributed to the diffusion of Pb²⁺ ions from water during drying. The relatively constant Pb/S ratio in the membrane interior confirms that adsorption instead of membrane exclusion is the dominant Pb²⁺ removal mechanism.

The regeneration ability of the MoS₂ membrane was evaluated by using EDTA cleaning to remove the adsorbed Pb²⁺ ions from the membrane after a filtration experiment. As shown in Figure 4d, the MoS₂ membrane adsorbed 0.15 mg Pb²⁺ from the first filtration cycle, and the EDTA cleaning by flushing with 80 mL EDTA solution recovered approximately 0.136 mg Pb²⁺ from the membrane, leading to a recovery of more than 90 %. It is worth noting that the concentration of recovered Pb²⁺ in the first 20 mL EDTA solution was as high as 5.5 mg/L, demonstrating the effectiveness in regenerating MoS₂ membranes. A second filtration cycle was performed after EDTA cleaning, and the regenerated MoS₂ membrane could reduce Pb²⁺ concentration to less than 10 µg/L with a treatment capacity of 90 mL, equivalent to nearly 90% of the original treatment capacity of a fresh MoS₂ membrane.

The treatment capacity of a POU filter is calculated by considering a conservative 65.6 mg/g lead removal capacity of the MoS₂ membrane (based on the tests shown in Figure S12). As shown in Figure 4e, the POU device demonstrates a treatment capacity of 63 to 625 L-water/g-MoS₂ depending on the initial Pb²⁺ concentration in tap water. For instance, when Pb²⁺

concentration in the water is 100 and 250 $\mu\text{g/L}$, a POU device containing 1 g of MoS_2 membrane could effectively treat 625 and 170 L water, respectively. The treatment capacity of MoS_2 membrane is several orders of magnitude higher than that of adsorptive membranes made of commercial or lab-synthetic materials reported in the literature^{12, 58, 59}. The superb performance can be attributed to the high adsorption capacity and selectivity of MoS_2 nanosheets as well as the fully accessible sulfur sites in the 1.2-nm 2D nanochannels enabled by the layer-stacking structure.

The leaching of MoS_2 nanosheets and soluble Mo species from MoS_2 membranes is also characterized in the filtration experiments. During the Pb adsorption and EDTA cleaning process, we observed a low concentration of leached Mo species ($< 0.1 \text{ mg/L}$) in the filtrate (Figure S13). This is due to the slow oxidation of chemically exfoliated MoS_2 to soluble molybdate ions as was reported previously.⁶⁰ To the best of our knowledge, molybdate ions have not been reported to generate environmental toxicity or negative human health impacts at such low concentrations. The leaching problem can also be potentially addressed by using more stable MoS_2 prepared by ultrasonication, which significantly slows down Mo leaching (Figure S13). Loose nanosheets were not observed throughout all filtration tests, nor during a batch test where external pressure was removed, a condition that can accelerate nanosheet release if applicable (Figure S14). This structural stability is consistent with our previous finding that the strong vdW forces between MoS_2 nanosheets could potentially prevent the layer-stacked MoS_2 nanosheets from releasing in water.⁴¹

Environmental Implications. Our findings suggest that emerging 2D MoS_2 nanosheets can find important applications like lead removal from drinking water. MoS_2 's superb lead adsorption

capabilities are evidenced by its adsorption capacity (740 mg/g) and its extremely high distribution coefficient K_d (5.2×10^7 mL/g), both of which are among the highest for materials that have ever been reported to the best of our knowledge. Additionally, once assembled into a layer-stacked membrane, the unique 1.2-nm 2D nanochannels formed between MoS₂ nanosheets make all the surface sulfur sites fully accessible for lead adsorption, while allowing water to permeate through the membrane at a fast speed. The layer-stacked MoS₂ membrane could effectively remove Pb²⁺ in drinking water from a few mg/L to less than 10 µg/L, with a treatment capacity a few orders of magnitude higher than that of membrane filters fabricated with commercial or other nanomaterials. An additional advantage of the MoS₂ membrane is that the nanochannels also enable the rejection of lead-containing particulates, a common form of lead contamination in tap water due to the corrosion of drinking water distribution pipes.⁶¹ MoS₂ has also been reported to have excellent antimicrobial/antifouling properties,^{62, 63} another important feature for multifunctional membrane applications. With exfoliation and synthesis methodology maturing, the cost and complexity of MoS₂ nanosheet production is expected to continuously decrease. Therefore, we believe that MoS₂ membrane-based technology holds great promise as a POU device installed in households, schools, or public utilities to remediate lead contamination and safeguard drinking water quality for the public.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. This document includes additional characterization of MoS₂ nanosheets and membranes, supplementary adsorption results, DFT modeling process and results.

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