

Fabrication of Ultrathin MoS₂ Nanosheets and Application on Adsorption of Organic Pollutants and Heavy Metals

Authors:

Siyi Huang, Ziyun You, Yanting Jiang, Fuxiang Zhang, Kaiyang Liu, Yifan Liu, Xiaochen Chen, Yuancai Lv

Date Submitted: 2020-07-02

Keywords: quenching, Adsorption, liquid exfoliation, transition metal dichalcogenides

Abstract:

Owing to their peculiar structural characteristics and potential applications in various fields, the ultrathin MoS₂ nanosheets, a typical two-dimensional material, have attracted numerous attentions. In this paper, a hybrid strategy with combination of quenching process and liquid-based exfoliation was employed to fabricate the ultrathin MoS₂ nanosheets (MoS₂ NS). The obtained MoS₂ NS still maintained hexagonal phase (2H-MoS₂) and exhibited evident thin layer-structure (1-2 layers) with inconspicuous wrinkle. Besides, the MoS₂ NS dispersion showed excellent stability (over 60 days) and high concentration (0.65 ± 0.04 mg mL⁻¹). The MoS₂ NS dispersion also displayed evident optical properties, with two characteristic peaks at 615 and 670 nm, and could be quantitatively analyzed with the absorbance at 615 nm in the range of 0.01-0.5 mg mL⁻¹. The adsorption experiments showed that the as-prepared MoS₂ NS also exhibited remarkable adsorption performance on the dyes (344.8 and 123.5 mg g⁻¹ of qm for methylene blue and methyl orange, respectively) and heavy metals (185.2, 169.5, and 70.4 mg g⁻¹ of qm for Cd²⁺, Cu²⁺, and Ag⁺). During the adsorption, the main adsorption mechanisms involved the synergism of physical hole-filling effects and electrostatic interactions. This work provided an effective way for the large-scale fabrication of the two-dimensional nanosheets of transition metal dichalcogenides (TMDs) by liquid exfoliation.

Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version):

LAPSE:2020.0771

Citation (this specific file, latest version):

LAPSE:2020.0771-1

Citation (this specific file, this version):


LAPSE:2020.0771-1v1

DOI of Published Version: <https://doi.org/10.3390/pr8050504>

License: Creative Commons Attribution 4.0 International (CC BY 4.0)

Article

Fabrication of Ultrathin MoS₂ Nanosheets and Application on Adsorption of Organic Pollutants and Heavy Metals

Siyi Huang¹, Ziyun You¹, Yanting Jiang¹, Fuxiang Zhang¹, Kaiyang Liu¹, Yifan Liu¹, Xiaochen Chen¹ and Yuancai Lv^{1,2,*} 

¹ Fujian Provincial Engineering Research Center of Rural Waste Recycling Technology, College of Environment & Resources, Fuzhou University, Fuzhou 350116, China; N170620033@fzu.edu.cn (S.H.); 061700527@fzu.deu.cn (Z.Y.); 061700506@fzu.deu.cn (Y.J.); 061700529@fzu.deu.cn (F.Z.); liukaiyang123@hotmail.com (K.L.); yfanym@fzu.edu.cn (Y.L.); chenxiaochen@fzu.edu.cn (X.C.)

² Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350116, China

* Correspondence: yclv@fzu.edu.cn; Tel.: +86-135-6003-1596

Received: 10 April 2020; Accepted: 24 April 2020; Published: 26 April 2020



Abstract: Owing to their peculiar structural characteristics and potential applications in various fields, the ultrathin MoS₂ nanosheets, a typical two-dimensional material, have attracted numerous attentions. In this paper, a hybrid strategy with combination of quenching process and liquid-based exfoliation was employed to fabricate the ultrathin MoS₂ nanosheets (MoS₂ NS). The obtained MoS₂ NS still maintained hexagonal phase (2H-MoS₂) and exhibited evident thin layer-structure (1–2 layers) with inconspicuous wrinkle. Besides, the MoS₂ NS dispersion showed excellent stability (over 60 days) and high concentration (0.65 ± 0.04 mg mL⁻¹). The MoS₂ NS dispersion also displayed evident optical properties, with two characteristic peaks at 615 and 670 nm, and could be quantitatively analyzed with the absorbance at 615 nm in the range of 0.01–0.5 mg mL⁻¹. The adsorption experiments showed that the as-prepared MoS₂ NS also exhibited remarkable adsorption performance on the dyes (344.8 and 123.5 mg g⁻¹ of q_m for methylene blue and methyl orange, respectively) and heavy metals (185.2, 169.5, and 70.4 mg g⁻¹ of q_m for Cd²⁺, Cu²⁺, and Ag⁺). During the adsorption, the main adsorption mechanisms involved the synergism of physical hole-filling effects and electrostatic interactions. This work provided an effective way for the large-scale fabrication of the two-dimensional nanosheets of transition metal dichalcogenides (TMDs) by liquid exfoliation.

Keywords: transition metal dichalcogenides; liquid exfoliation; adsorption; quenching

1. Introduction

Given the special structure and potential applications, two-dimensional materials have drawn plenty of concerns [1,2], such as graphene, boron nitride, and molybdenum disulfide. Among them, the ultrathin molybdenum disulfide (MoS₂) nanosheets, which exhibit an evident layered structure, have attracted ample attentions because of their excellent performance on several fields, such as catalysis, sensors, and pollution remediation [1,3]. Recently, the ultrathin MoS₂ nanosheets were reported to show excellent prospects in pollution control [3,4]. Therefore, it was urgent to explore an effective method to produce ultrathin MoS₂ nanosheets.

To date, a few methods have been reported for efficient preparation of ultrathin MoS₂ nanosheets [5–10], for example, mechanical exfoliation, sputtering, atomic layer deposition, chemical methods, and liquid-based exfoliation. In spite of the excellent performance of the prepared monolayer or few-layer MoS₂ nanosheets through mechanical methods, the production efficiency was rather low, which severely limited the large-scale applications. Meanwhile, although most of the chemical

methods like hydrothermal and solvent thermal routes could produce large-scale few-layer MoS₂ nanosheets, they generally needed strict reaction control, such as high temperature and pressure. Instead, due to the controllable operation and high production, liquid-based exfoliation was regarded as the most promising way for the production of ultrathin MoS₂ in large scale. According to previous studies [7,8], the solvent showed a significant impact on the exfoliation of MoS₂. Among which, pyrrolidone-based solvents like *N*-methyl-2-pyrrolidone displayed excellent MoS₂ exfoliation efficiency with 0.3 mg mL⁻¹ of MoS₂ nanosheets concentration, because they showed similar surface energy with MoS₂. Nevertheless, considering their significant environmental risk, high toxicity and high-boiling points of the pyrrolidone-based solvents probably limited the large-scale application. To replace these toxic solvents, a number of polar solvents that own low boiling point and molecular weight were tested, such as water, methanol, ethanol, and isopropanol [11,12]. Unfortunately, given the different surface energy between the MoS₂ and polar solvents, most of the polar solvents showed dissatisfactory exfoliation efficiency [11]. Interestingly, it was reported that the MoS₂ exfoliation efficiency in the mixed solution with two of the polar micromolecular solvents was much better than those in the single solvent [13,14]. Meanwhile, it was worth noting that the MoS₂ exfoliation efficiency could be significantly improved when some organic small molecules, surfactants, or polymers were added in the polar micromolecular solvents, such as sodium cholate, Tween 80, Tween 85, sodium naphthalenide, Brij 30, Brij 700, Triton X-100, and so on [15–17]. Nevertheless, the strong van der Waals interaction between the MoS₂ layers still limited the MoS₂ nanosheets production.

Recently, owing to the effective break of the van der Waals force between the MoS₂ layers, quenching was found to be an effective way to exfoliate the graphene analogues [18–21]. Previous investigation showed that the high-quality ultrathin graphene sheets were fabricated by rapidly cooling the hot bulk graphite and pre-expanded graphite in aqueous solutions of NH₄HCO₃ and hydrazine hydrate, respectively [19,20]. Meanwhile, the boron nitride and MoS₂ nanosheets were also synthesized via the rapid quenching of hot bulk boron nitride and MoS₂ in the liquid N₂ [18,21]. Although the production efficiency of the nanosheets was dissatisfactory, we suspect that if the bulk MoS₂ was pretreated with the quenching process, the exfoliation efficiency of MoS₂ nanosheets in the polar micromolecular solvents could be significantly improved.

Herein, a hybrid strategy with the combination of quenching process and liquid-based exfoliation was employed to fabricate the ultrathin MoS₂ nanosheets. The microstructures, morphology, and optical properties were analyzed. In addition, the adsorption performance of dyes and heavy metals was also discussed.

2. Material and Methods

2.1. Materials

Ammonium tetrathiomolybdate ((NH₄)₂MoS₄) was provided by Sam Chemical Technology Co., Ltd. (Shanghai, China). Hydrazine monohydrate (N₂H₄·H₂O) was provided by Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), nitric acid (HNO₃), methylene blue (MB), methyl orange (MO), AgNO₃, CuSO₄, and CdCl₂ were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The double-distilled water was prepared with a Milli-Q water purification system (Milli-Q®Reference, Millipore, Billerica, Massachusetts, USA).

2.2. Fabrication of the MoS₂ Nanosheets

The MoS₂ nanosheets (MoS₂-NS) were prepared through a novel combined method including calcination at high temperature, quenching with liquid nitrogen, and ultrasonic-assisted peeling with hydrazine hydrate. Firstly, 4.000 g of (NH₄)₂MoS₄ was calcinated under nitrogen atmosphere at 800 °C for 5 h with a rate of 5 °C/min and then a black powder (named bulk MoS₂) was obtained. After that, the high-temperature bulk MoS₂ was quickly transferred into a Dewar bottle containing liquid nitrogen until the liquid nitrogen gasified completely. Subsequently, the pre-expanded bulk

MoS₂ was transferred into a serum bottle with 100 mL of hydrazine hydrate and the bottle was sonicated at a frequency of 40 kHz for 24 h. After centrifugation, the residual MoS₂ powders were added into another serum bottle with deionized water and sonicated for 12 h (In addition, the recycled hydrazine hydrate can be reused in a new procedure.). Finally, the resulting suspensions were centrifuged at 3000 rpm for 2 h and then the dark green MoS₂-NS dispersions were obtained. After dialyzed with dialysis tubing with 3000 dalton of molecular weight cut off, the obtained ultimate green dispersions were close to 7 of pH and stored in the fridge at 4 °C.

2.3. Adsorption Batch Experiments

Adsorption isotherm batch experiments were carried out in a 40-mL serum bottle containing 10 mL liquid with 0.1 g L⁻¹ of the adsorbent concentration. The adsorption isotherm for MB and MO was conducted under 25 °C in the range of 0.5 to 50 mg L⁻¹ of the MB and MO concentration and the pH was adjusted to 6.0 ± 0.1 with 1 M H₂SO₄ solution, while the experiments for heavy metals were conducted under 25 °C with metal concentration from 0.5 to 30 mg L⁻¹ and the pH was adjusted to 5.0 ± 0.1 with 1 M H₂SO₄ solution. After sealed with polytetrafluoroethylene (PTFE) caps, all the bottles were shaken at 250 rpm for 6 h. At sampling points, one bottle was taken out. After filtered with 0.22 µm glass fiber filters (Tianjin Branch billion Lung Experimental Equipment Co., Ltd., Tianjin, China), the MB/MO concentrations were determined by UV-vis spectroscopy (UV-1780, SHIMADZU, Japan) at 664/464 nm, while the residual Cu²⁺/Cd²⁺/Ag⁺ concentrations were analyzed with ICP-MS (XSERIES 2, Thermo). The adsorption isotherms data were treated with Langmuir and Freundlich models [22,23]. The experiments for the adsorption kinetics study were operated at 25 °C and 6.0 ± 0.1/5.0 ± 0.1 of pH (adjusted with 1 M H₂SO₄ solution) in 300 mL dyes/heavy metals solution (20 mg L⁻¹ for dyes and 15 mg L⁻¹ for heavy metals). All the samples were shaken at 250 rpm for 6 h. At sampling points, 1.5 mL of the solution was taken out and then filtered through the filters. The residual dyes/heavy metals concentrations were determined with ICP-MS. The adsorption kinetics data were treated with the pseudo-first order kinetic and pseudo-second-order non-linear kinetic models.

To study the effects of pH values (2–10)/(3–7) on dyes/heavy metals adsorption, the batch experiments were conducted at 25 °C in a serum bottle with 20 mg L⁻¹/15 mg L⁻¹ of dyes/heavy metals concentration and 0.10 g L⁻¹ of adsorbents.

2.4. Characterization

The X-ray powder diffraction (XRD) data of the bulk MoS₂ and MoS₂-NS were tested with X-ray powder diffractometer (MiniFlex600, Rigaku, Milwaukee, Wisconsin, USA) coupled with a Cu K α line at 40 kV and 40 mA.

The microstructural features of prepared bulk MoS₂ and MoS₂-NS were observed with field emission scanning electron microscope (FESEM, Nova NanoSEM 230, FEI, Hillsboro, Oregon, USA), atomic force microscope (AFM, 5500, Agilent USA), and transmission electron microscope (TEM, TECNAI G2F20, FEI, Hillsboro, Oregon, USA).

The Raman data of bulk MoS₂ and MoS₂-NS were recorded by a confocal laser Raman microscopy (Invia Reflex, Renishaw, UK) with 532 nm of laser wavelength and 0.6 mW of laser energy.

The X-ray photoelectron spectroscopy (XPS) data were recorded with X-ray photoelectron spectrometer (ESCALAB 250, Thermo Scientific, Waltham, Massachusetts, USA) coupled with the Al K α radiation at 15 kV and 51 W. The binding energies were confirmed by using the C1s component as the reference and the binding energy of C-C/H bonds were set at 284.5 eV.

The concentrations of MoS₂-NS dispersions were analyzed using UV-vis spectrophotometer (UV-2500, Shimadzu, Japan).

The Brunauer–Emmett–Teller (BET) surface areas of the bulk MoS₂ and MoS₂-NS were obtained from the analysis of N₂-adsorption isotherms at 77 K using the N₂ physisorption analyzer (ASAP2020, Micromeritics, Norcross, Georgia, USA).

3. Results and Discussion

3.1. Characterization of MoS₂ Nanosheets

3.1.1. Microstructures and Morphology

To study the variation of the crystal structure during the MoS₂-NS preparation, the precursor ((NH₄)₂MoS₄), bulk MoS₂ and MoS₂-NS were analyzed by XRD and the results were illustrated in Figure 1. As shown in Figure 1, after calcination under N₂, the characteristic peaks of (NH₄)₂MoS₄, located at $2\theta = 17.2^\circ$, 18.44° , and 29.08° , fully vanished, suggesting the evident change of crystal structure. Instead, the peaks at $2\theta = 14.6^\circ$, 33.48° , 39.82° , and 58.94° were assigned to the (100), (103), (105), and (110) plane of hexagonal MoS₂ phase (JCPDS card No. 65-0160), indicating that after calcination, the obtained bulk MoS₂ was hexagonal phase. The results were similar to Zhang et al.'s findings [24,25]. In addition, after exfoliation by sonication, the resulting MoS₂-NS still kept the same peaks with bulk MoS₂, manifesting that the 2H-MoS₂-NS was successfully obtained. However, compared to the bulk MoS₂, the (002) plane peak of MoS₂-NS became broadened and lower, suggesting an increase of the *d* spacing between MoS₂ layers [26]. Based on the full width at half maximum (FWHM) of the (002) plane, the layer number of the prepared MoS₂-NS could be calculated to be about ~2 layers through Scherrer's equation. To further confirm the structure of the exfoliated MoS₂-NS, Raman spectroscopy (Figure 1b) was employed to characterize the bulk MoS₂ and MoS₂-NS. Both the bulk MoS₂ and MoS₂-NS exhibited two dominant peaks ranging from 340 to 450 cm⁻¹, corresponding to the E_{12g}¹ and A_{1g} mode of the hexagonal MoS₂, respectively [26,27], which convincingly proved the successful exfoliation of MoS₂-NS. Among which, the E_{12g}¹ mode peak at 381.6 cm⁻¹ involved the in-layer displacements of Mo and S atoms, whereas the A_{1g} mode peak at 407.9 cm⁻¹ represented the out-of-layer symmetric displacements of S atoms along the *c*-axis [28]. Noticeably, compared to the bulk MoS₂, the E_{12g}¹ (377.8 cm⁻¹) and A_{1g} (402.2 cm⁻¹) mode peaks displayed evident blue shift, and the interval ($\Delta = 24.4$ cm⁻¹) between E_{12g}¹ and A_{1g} peaks was lower than that of bulk MoS₂ ($\Delta = 26.3$ cm⁻¹), which was ascribed to the decrease of the MoS₂ thickness. According to the previous literature [4,25,29], it was found that both E_{12g}¹ and A_{1g} peaks were the characteristic peaks of MoS₂ and their frequencies would vary with the layer number. When the layer number increases, the interlayer van der Waals force in MoS₂ suppressed atom vibration, resulting in higher force constants [30]. On the contrast, the force constants between the layers would weaken with the layer number decreases. Thus, both E_{12g}¹ and A_{1g} modes were supposed to stiffen (blue-shift) along with the reduction of MoS₂ layers.

Figure 2a–d presented the FESEM images of the bulk MoS₂ and MoS₂-NS. As seen in Figure 2a,b, the bulk MoS₂ displayed varisized particle-like morphology but clearly thick layer-structure. After exfoliation, the MoS₂-NS exhibited evident thin layer-structure with inconspicuous wrinkle (Figure 2c,d), which suggested the successful exfoliation of MoS₂-NS. Similar to the bulk MoS₂, the size of prepared MoS₂-NS still differed widely. In addition, the thickness of the prepared MoS₂-NS was analyzed by atomic force microscopy (AFM) (Figure 2). As seen in the AFM images (Figure 2e,f), the height profile of the two selected regions displayed a height of ~1.20 nm (± 0.03 nm) for MoS₂-NS, which was about 2 times as thick as the theoretical thickness of monolayer MoS₂ (~0.65 nm) [27]. The evident platform of the height curves of the selected MoS₂-NS revealed the smooth surface for MoS₂-NS. Low-resolution TEM image (Figure 2g) also clearly depicted well-stacked layered structures (~2 layers) of the MoS₂-NS, which strongly confirmed the results of XRD and AFM. In the high-resolution TEM (HRTEM) images (Figure 2h), the lattice spacing of 0.27 and 0.16 nm between two adjacent lattice planes could be resolved, which were assigned to the (100) and (110) plane of MoS₂. In addition, the HRTEM image (Figure 2i) and associated fast Fourier transforms (FFT) (Figure 2j) from the center of the MoS₂-NS evidently exhibited hexagonally symmetric structure, which was consistent with the results of XRD analysis. All the above results manifested that the obtained MoS₂-NS still retained hexagonal single crystalline nature during pre-expansion and sonication treatments, which agreed with the previous findings [25,31,32]. However, the BET analysis (Figure 3) showed that the specific

surface areas of bulk MoS₂ and MoS₂-NS were 5.6 and 26.6 m² g⁻¹, respectively, indicating that the exfoliation greatly changed the specific surface area of the MoS₂ materials. With the decreasing of the layers, more and more MoS₂ was exposed, resulting in a promotion of the BET surface.

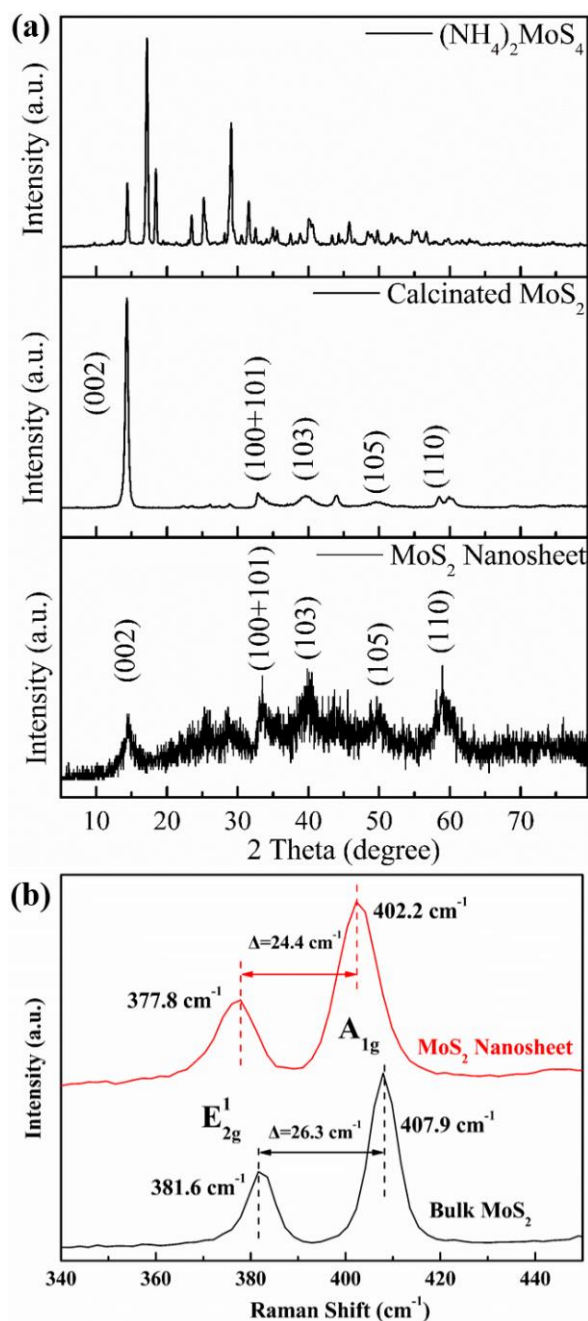


Figure 1. (a) XRD patterns of (NH₄)₂MoS₄, bulk MoS₂, and MoS₂-NS and (b) Raman spectra of bulk MoS₂ and MoS₂ nanosheets.

The chemical composition and element valence on the surface of MoS₂ NS were analyzed with XPS (Figure 4). As depicted in Figure 4a, the survey spectra clearly confirmed the presence of C, O, NS, and Mo elements. The weak C1s (~284 eV) peak was attributed into the calibration of binding energy with carbon, while the N1s (~400 eV) peak was ascribed into the adsorbed hydrazine hydrate during the sonication. In Mo3d core-level spectra (Figure 4b), the appearance of Mo3d_{5/2} (233.5 eV) and Mo3d_{3/2} (232.6 eV) peaks for Mo3d doublet indicated the characteristic +4 oxidation state [1]. Besides, two weak Mo⁶⁺ 3d peaks (3d_{5/2} peak at 233.5 eV and 3d_{3/2} peak at 235.9 eV) were ascribed to

the slight oxidation of MoS₂ NS edge during the MoS₂ transfer under high temperature [25]. In the high-resolution scans of S2p (Figure 4c), two feature peaks (S2p1/2 and S2p3/2) were observed at 162.0 and 163.3 eV, respectively, which greatly matched the binding energy of S²⁻ ions in 2H-MoS₂ [2]. In addition, the appearance of O1s also confirmed the oxidation of MoS₂. In the high-resolution spectra of O1s (Figure 4d), the peak of O²⁻ species located at 532.0 eV and the peak at 533.5 eV was attributed into the absorbed oxygen-containing material like H₂O [3].

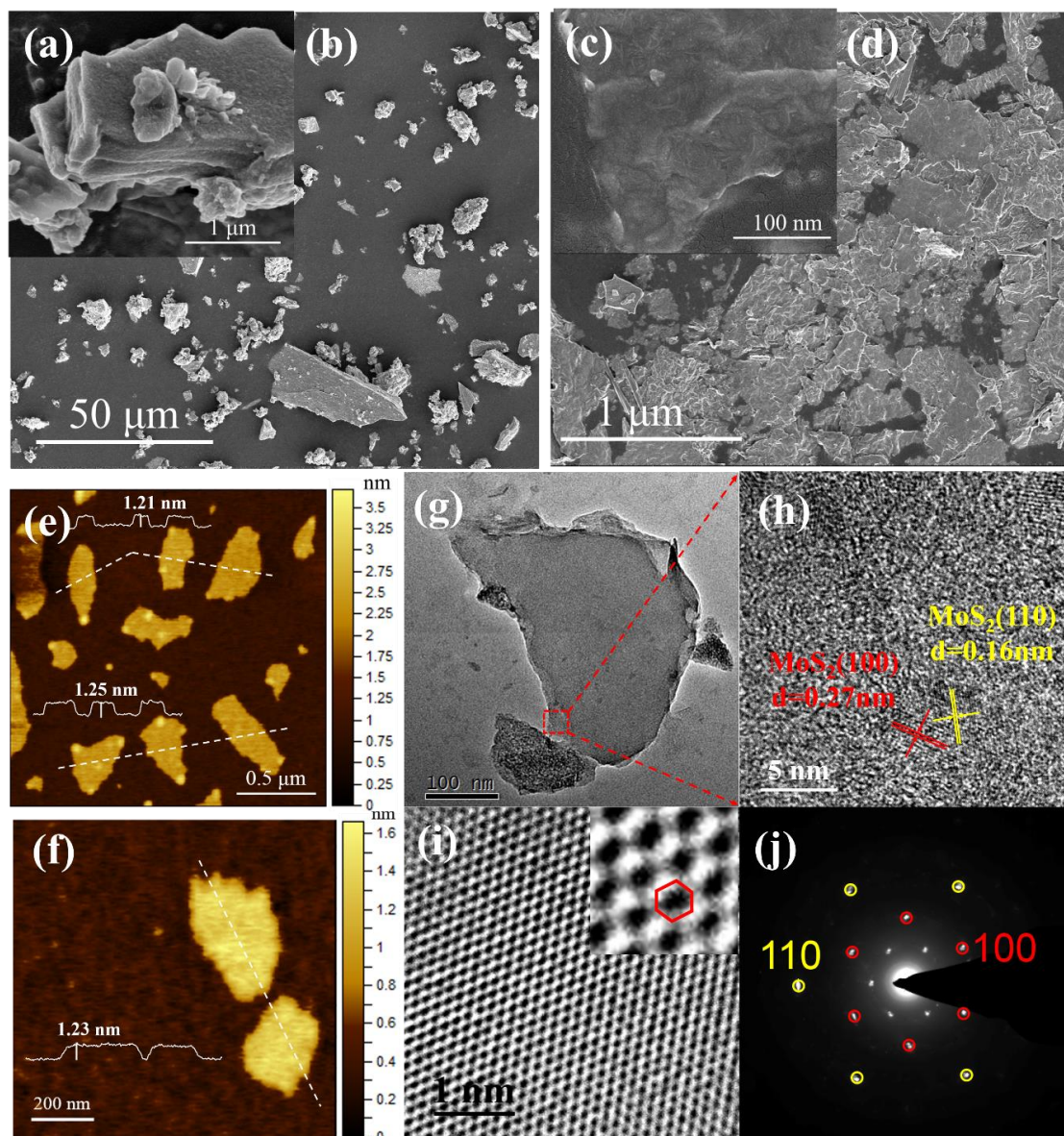


Figure 2. Field emission scanning electron microscope (FESEM) images (a–d) of the bulk MoS₂ and MoS₂-NS, atomic force microscope (AFM) images (e,f), height profiles (inset), (transmission electron microscope) TEM and high-resolution transmission electron microscope (HRTEM) images of MoS₂ nanosheets (g–i), and the fast Fourier transforms (FFT) pattern of MoS₂ NS (j).

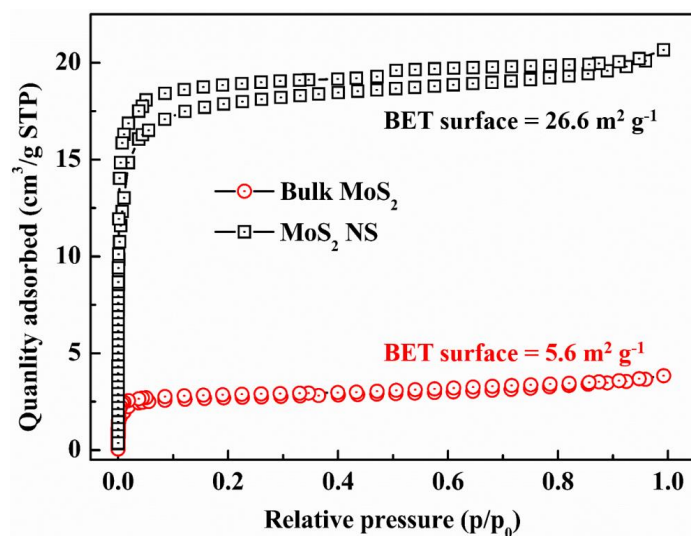


Figure 3. Brunauer–Emmett–Teller (BET) N₂ isotherms of the bulk MoS₂ and MoS₂ NS.

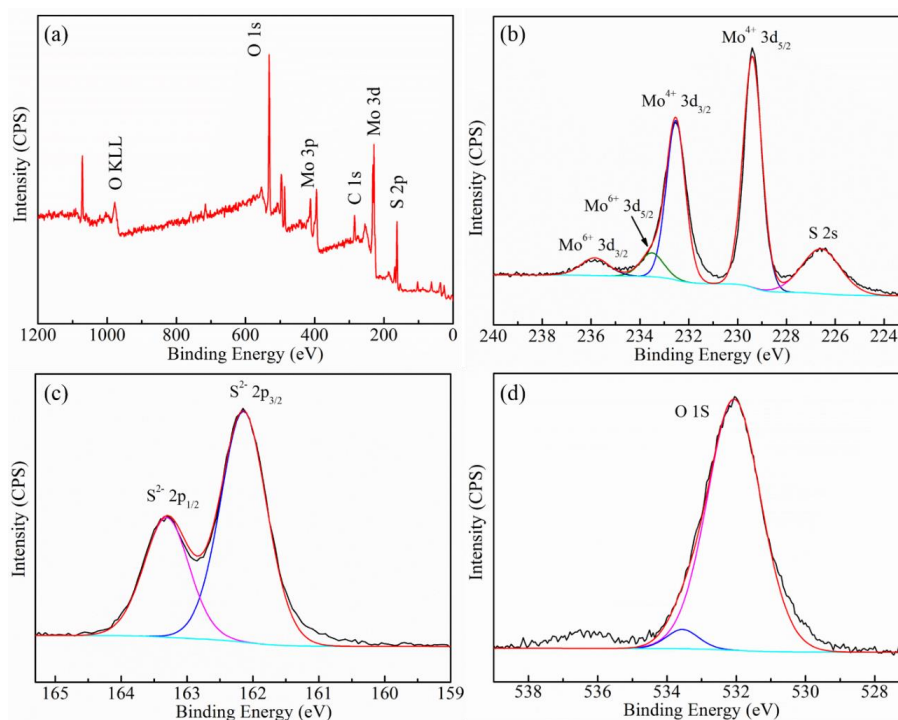


Figure 4. XPS survey spectra of MoS₂ (a) and high-resolution scans of Mo3d (b), S2p (c), O1s (d).

3.1.2. Optical Properties of MoS₂ Nanosheets Dispersion

To obtain pure few-layer MoS₂ NS, the suspensions were first centrifuged at 3000 rpm for 2 h to remove the no exfoliated precipitate. Figure 5a displayed the photographs of the as-prepared MoS₂ NS in water. As shown in the Figure 5a, the evident Tyndall phenomenon was observed both of the fresh MoS₂ NS dispersions and the dispersions after 60 days. Meanwhile, the UV-vis absorption spectra (Figure 5b,c) also exhibited no evident change during 60 days. All the results suggested the excellent stability (stable for over 60 days) of as-prepared MoS₂ NS dispersions. In addition, the UV-vis absorption spectra (Figure 5e) of the resulting MoS₂ NS dispersions with different concentrations (Figure 5d) displayed two distinctly characteristic peaks for 2H-MoS₂ [33]. The two peaks located at 615 (B-exciton) and 670 nm (A-exciton) were attributed to the direct excitonic transitions of MoS₂ at the

K point of the Brillouin zone [34,35]. According to Hai et al.'s study [25], the relationship between the concentrations of MoS₂ NS dispersions and the measured absorbance at a given wavelength (615 or 670 nm) were estimated by using the Beer–Lambert law. The fitting results (Figure 5f) proved that the concentrations of the dispersions showed good linear relationship ($R^2 = 0.9996$) with the absorbance at 615 nm in the range of 0.01–0.5 mg L⁻¹, which meant that the quantitative analysis of the MoS₂ NS dispersions was available. Based on the above relationship, the concentration of the as-prepared MoS₂ NS dispersions was 0.65 ± 0.04 mg mL⁻¹, which was much higher than previous findings [7,25]. The initial concentration of the bulk MoS₂ (2.510 g of bulk MoS₂ were obtained after the calcination of (NH₄)₂MoS₄) was 2.51 mg mL⁻¹, and the corresponding few-layer MoS₂ NS yield was calculated to be as high as 25.9% in water.

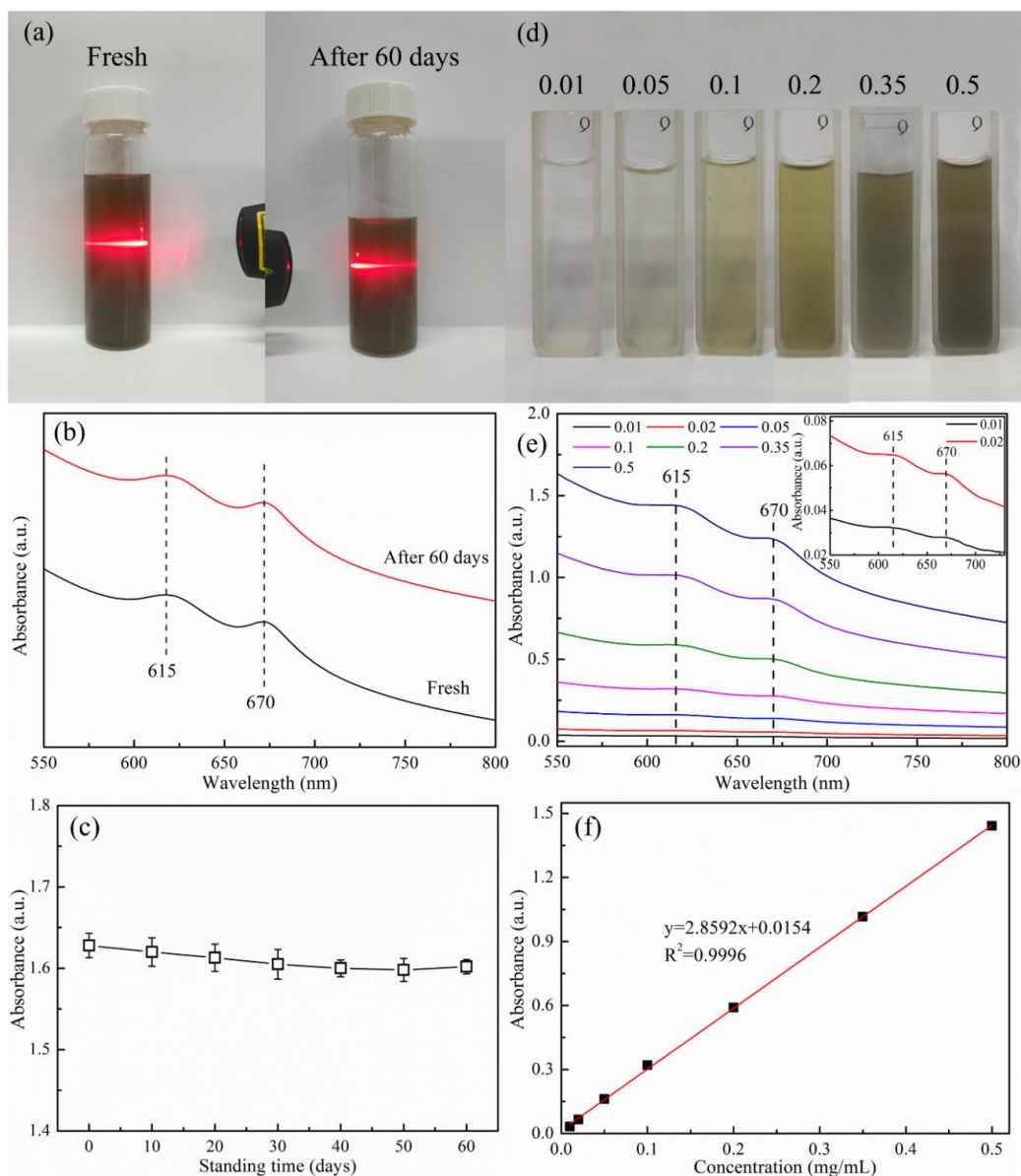


Figure 5. Photographs (a), UV-vis absorption spectra (b), absorbance change with standing time (c) of the prepared MoS₂ NS dispersions and photographs (d), UV-vis absorption spectra (e) and standard curve (f) of MoS₂ NS dispersion in different concentrations.

3.2. Adsorption Behavior of MoS₂-NS Towards Dyes and Heavy Metals

3.2.1. Adsorption Isotherms and Kinetics

The adsorption performance of the MoS₂ NS was tested by selecting two dyes (methylene blue, MB and methyl orange, MO) and three heavy metal ions (Cu²⁺, Cd²⁺, and Ag⁺) as the targets. As seen in Figure 6a, in the bulk MoS₂ systems, the equilibrium adsorption capacities of the two dyes only slightly increased with the increasing of the dye concentrations, manifesting that the bulk MoS₂ exhibited unsatisfactory adsorption performance of MB and MO. Instead, the equilibrium adsorption capacities of MoS₂ NS for MB and MO significantly increased under high concentration of dyes, which were much larger than those of bulk MoS₂. Meanwhile, the as-prepared MoS₂ NS also displayed more excellent adsorption performance on heavy metals than the bulk MoS₂. All the results indicated that the exfoliation was beneficial to improve the adsorption performance of MoS₂, which was in accordance with previous studies [3,36,37].

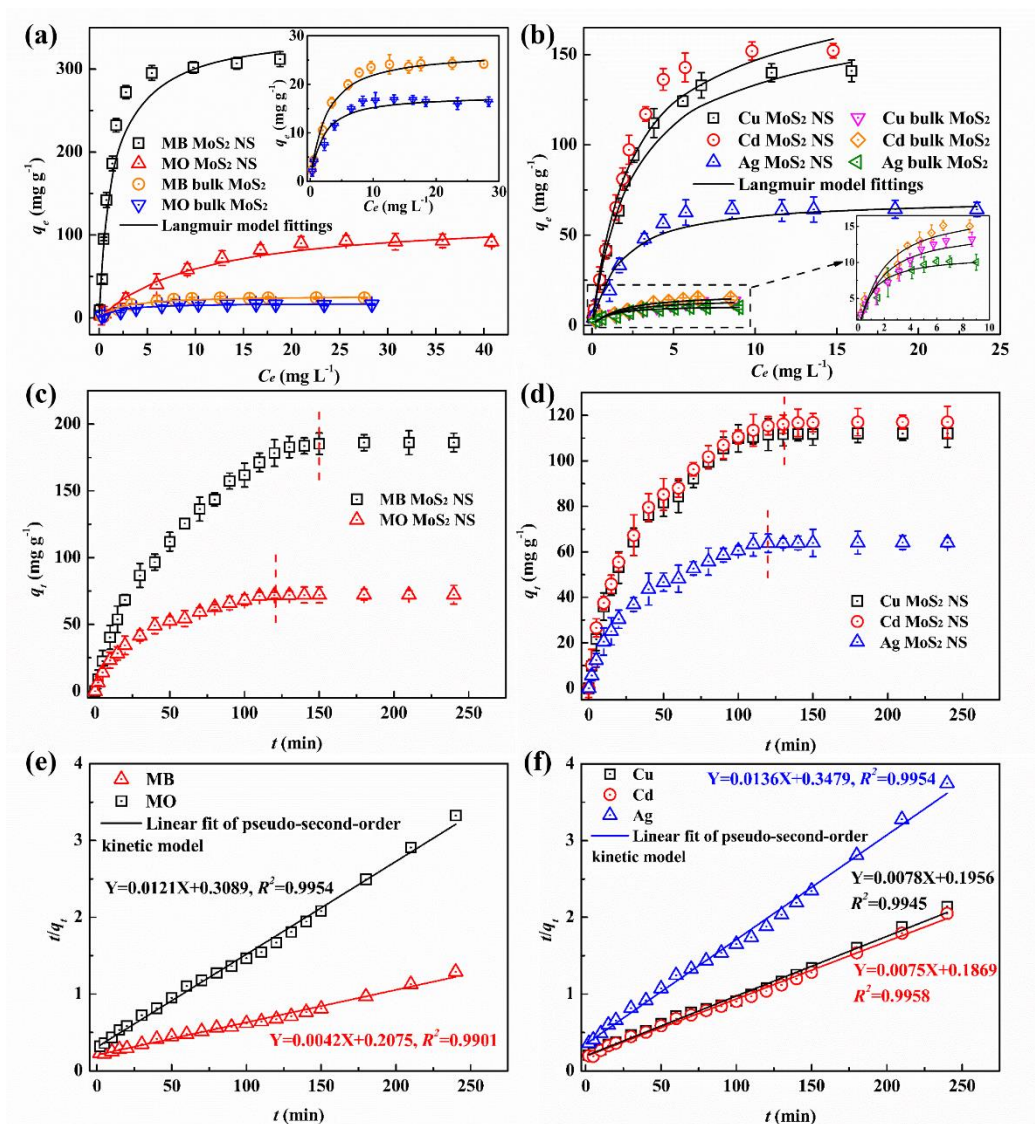


Figure 6. Adsorption isotherms (a) and kinetics (c,e) of MB, MO for bulk MoS₂ and MoS₂ NS at 20 mg L⁻¹; adsorption isotherms (b) and kinetics (d,f) of Cu²⁺, Cd²⁺ and Ag⁺ for bulk MoS₂ and MoS₂ NS at 15 mg L⁻¹.

In addition, to well study the adsorption behavior, the Langmuir and Freundlich models were employed to fit the experimental data (Figure 6a,b, Figure S1). As listed in Table 1, the high R^2 values suggested that the Langmuir model better described the adsorption of dyes and heavy metals onto MoS₂ NS and bulk MoS₂ than the Freundlich model. Based on the Langmuir model fitting, the relative parameters like the maximum adsorption capacity (q_m) and affinity constant (K_L) for dyes and heavy metals were obtained and listed in Table 1. The q_m values of MB and MO for MoS₂ NS were 344.8 and 123.5 mg g⁻¹, respectively, which were 12.77 and 6.94 larger than those (27.0 and 17.8 mg g⁻¹ for MB and MO, respectively) of bulk MoS₂. Meanwhile, the similar results were observed in the heavy metal adsorption, indicating that the MoS₂ NS exhibited much more excellent adsorption performance than the bulk MoS₂. In addition, for the dyes, the higher q_m and K_L values of MB implied that MoS₂ materials exhibited better adsorption capacity and affinity to MB. For heavy metals, the highest q_m value occurred to Cd²⁺ (185.2 mg g⁻¹), following Cu²⁺ (169.5 mg g⁻¹) and Ag⁺ (70.4 mg g⁻¹), indicating that MoS₂ NS were more beneficial to Cd²⁺ and Cu²⁺ adsorption than Ag⁺.

Table 1. Fitted parameters for the adsorption of dyes and heavy metals on MoS₂ NS and bulk MoS₂.

Samples	Targets	Langmuir Model			Freundlich Model		
		q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	$1/n$	K_f (L g ⁻¹)	R^2
MoS ₂ NS	MB	344.8	0.725	0.994	0.648	92.796	0.875
	MO	123.5	0.393	0.980	0.724	9.023	0.969
Bulk MoS ₂	MB	27.0	0.238	0.996	0.504	6.381	0.915
	MO	17.8	0.187	0.992	0.449	4.988	0.904
MoS ₂ NS	Cd ²⁺	185.2	0.606	0.985	0.708	40.496	0.943
	Cu ²⁺	169.5	0.588	0.989	0.693	35.848	0.938
	Ag ⁺	70.4	0.339	0.993	0.533	18.326	0.914
Bulk MoS ₂	Cd ²⁺	18.7	0.297	0.952	0.463	6.069	0.979
	Cu ²⁺	16.3	0.285	0.963	0.459	5.321	0.991
	Ag ⁺	11.7	0.134	0.987	0.389	4.913	0.968

Figure 6c,d displayed adsorption kinetics data for dyes and heavy metals over MoS₂ NS. As revealed in Figure 6c, both MO and MB adsorption increased rapidly at the beginning, then proceeded at a slower rate, and tended to equilibrium at the end. The similar results occurred to the adsorption of heavy metals. Besides, to further analyze the time-dependent variation during the adsorption process, pseudo-first-order and pseudo-second-order kinetic models were employed to fit the dyes and heavy metals adsorption on MoS₂ NS (Figure 6e,f). As shown in Table S1, the higher R^2 values suggested that the pseudo-second-order model better described both dyes and heavy metals adsorption than the pseudo-first-order model, suggesting that the electron transfer between MoS₂ NS and dye molecule or metal ions played a controlling role during the adsorption [38].

3.2.2. Adsorption Mechanism

Based on the results, the MoS₂ NS showed much better dye or metal adsorption performance than bulk MoS₂. According to the previous studies [3,37,39,40], the main mechanisms reported during the adsorption of dyes or metal by the inorganic materials involved physical hole-filling effects, electrostatic interactions, and ion exchange.

Physical Hole-Filling Effects

The specific surface area often displayed significant effect on the adsorption of the pollutants [41–43]. The adsorbents with large specific surface area usually owned abundant pores, which greatly provided a sufficient adsorption site to capture the pollutants, resulting in the promotion of their adsorption performance. For nano materials, the physical hole-filling effect was considered as one of the important

adsorption mechanisms [41]. According to above-mentioned results, the obtained MoS₂ NS owned much larger specific surface area than bulk MoS₂, while the MoS₂ NS also exhibited more excellent adsorption performance on dyes and heavy metals. Thus, it could be inferred that the physical hole-filling effect probably played a vital role in the promotion of dyes or heavy metal adsorption. Herein, to verify the role of specific surface area during the dyes or heavy metal adsorption over MoS₂ NS and bulk MoS₂, the obtained q_e data were standardized with the BET surface area and the results were showed in Figure 7. As shown in Figure 7a, for dyes, the equilibrium adsorption capacities of MoS₂ NS for MB and MO were 312.0 and 92.6 mg g⁻¹, which were 12.89 and 5.61 times larger than those of bulk MoS₂, respectively. Meanwhile, the as-prepared MoS₂ NS also displayed excellent adsorption performance on heavy metals (Figure 7c), with 141.0, 152.8, and 64.2 mg g⁻¹ for Cu²⁺, Cd²⁺, and Ag⁺, respectively, which were 10.68, 10.12, and 6.42 folds larger than those of bulk MoS₂ (13.2, 15.1, and 10.0 mg g⁻¹ for Cu²⁺, Cd²⁺, and Ag⁺, respectively). After standardization (Figure 7b,d), all of the q_e ratios between the MoS₂ NS and bulk MoS₂ significantly decreased from 12.89 (MB), 5.61 (MO), 10.12 (Cu²⁺), 10.68 (Cd²⁺), and 6.42 (Ag⁺) to 2.72, 1.12, 2.24, 2.11, and 1.33, respectively, suggesting that the physical hole-filling effect played positive role in the promotion of dyes or heavy metal adsorption over MoS₂.

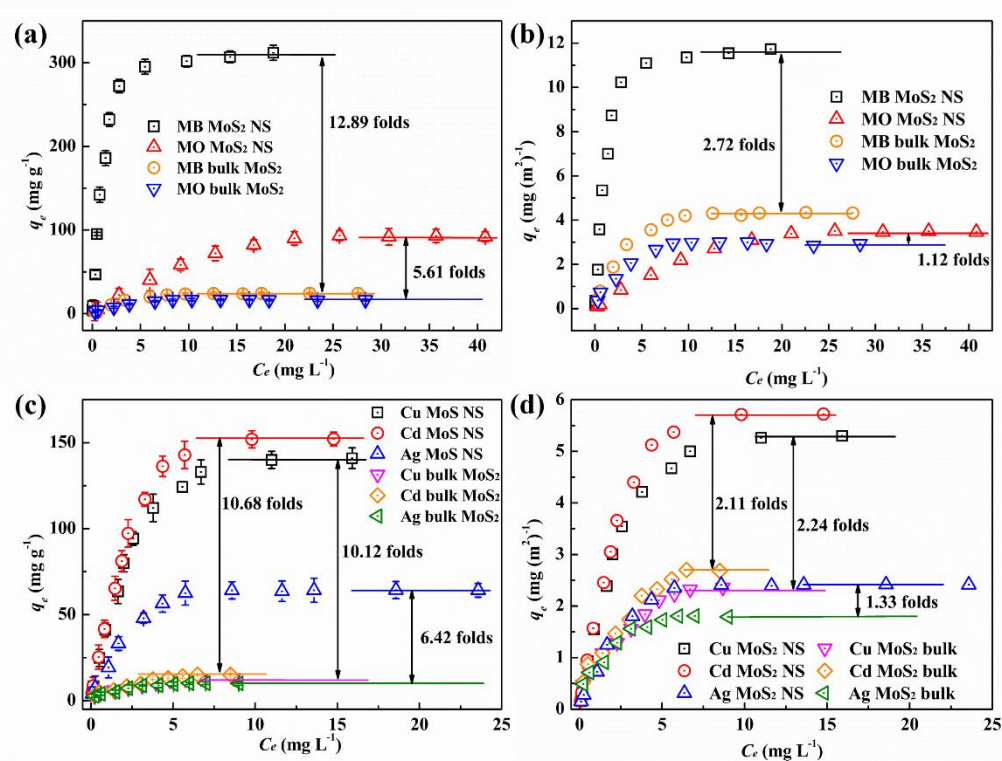


Figure 7. Equilibrium adsorption capacity (a,c) and standardized equilibrium adsorption capacity (b,d) of dyes (MO and MB) and heavy metals (Cu²⁺, Cd²⁺, and Ag⁺) for bulk MoS₂ and MoS₂ NS.

In addition, no evident variation was observed between the standardized q_e values of MoS₂ NS and bulk MoS₂ (Figure 7b), meaning that the physical hole-filling effect was the sole mechanism during MO adsorption over MoS₂ NS. However, the significant enhancement between the standardized q_e values of MoS₂ NS and bulk MoS₂ (Figure 7b,d) suggested that besides the physical hole-filling effect, some other mechanisms were involved during the adsorption of MB and heavy metals over MoS₂ NS.

Electrostatic Interactions

Electrostatic interaction was often considered as a possible mechanism to explain the adsorption of dyes and heavy metals [37,40,44]. To confirm the role of electrostatic interaction during dyes and

heavy metals adsorption over MoS₂ NS, the adsorption efficiency in various pH values were conducted. As depicted in Figure 8a, the slight fluctuation among the q_e values for MO suggested that the MB adsorption over MoS₂ NS was not controlled by the pH values. Instead, the MB adsorption was notably influenced by the pH values. At low pH (<6) conditions, the q_e values increased with the pH value and reached a peak (186.2 mg g⁻¹) at pH = 6.0, and then gradually declined when pH > 6. Meanwhile, Zeta potential results (Figure 8c) showed that the isoelectric point of MoS₂ NS was about 3.8. This meant that the surface of MoS₂ NS displayed a positive charge when the pH value was below 3.8, while a negative charge above 3.8. As a typical cationic dye, MB molecules could strongly adhere to the MoS₂ NS through the electrostatic interaction once the surface charge of MoS₂ NS turned to negative, leading to an increasing of the q_e values.

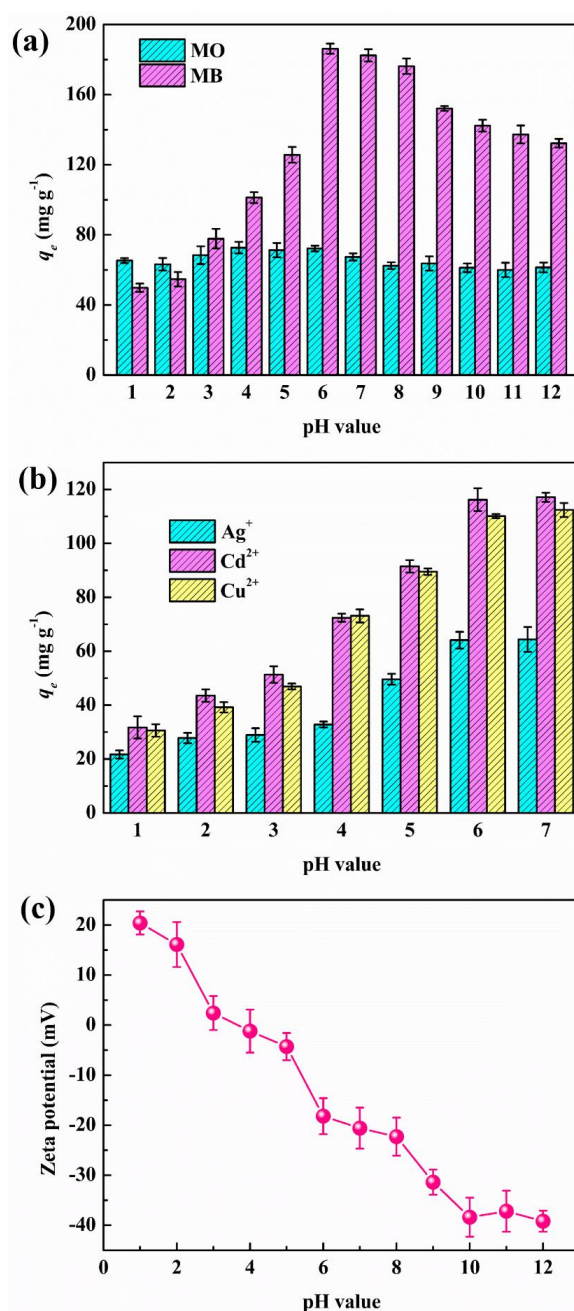


Figure 8. Effects of pH on dyes (a) and heavy metals (b) over MoS₂ NS, and the Zeta potential (c) of MoS₂ NS at different pH values. For dyes: 20 mg L⁻¹ of the initial concentration, for heavy metals: 15 mg L⁻¹ of the initial concentration.

Similarly, the pH also markedly influenced the adsorption of heavy metals over MoS₂ NS (Figure 8b). The q_e values of Cu²⁺, Cd²⁺, and Ag⁺ evidently increased with an increasing pH, and stabilized at about 112.4, 117.0, and 64.4 mg g⁻¹, respectively. When the pH increased, the surface charge of MoS₂ NS turned to negative and the values gradually increased, which meant that stronger electrostatic interaction occurred between the heavy metal ions and MoS₂ NS at higher pH, resulting in improvement of the adsorption performance. In addition, the charge values of the heavy metal ions also showed visible effects on the adsorption capacity. Due to the lower value of the charge for Ag⁺, the q_e value of Ag⁺ was much lower than those of Cu²⁺ and Cd²⁺, which was ascribed into the weaker electrostatic interaction between Ag⁺ and MoS₂ NS. According to the Coulomb law, electrostatic interaction was in direct proportion to the value of the surface charge. The similar results were also found in Yang et al.'s studies [45].

Ion Exchange

According to previous studies [43,46], the ion exchange only occurred with heavy metals adsorption. It was well known that the affinity to the metal ions in the ion exchange process increased with the ion radius and the ion radius of Cd²⁺ and Cu²⁺ were 0.97 Å and 0.73 Å, respectively. If the ion exchange was the main adsorption mechanism, the number of the adsorbed Cd²⁺ should be larger than that of Cu²⁺. Actually, in the system of 15 mg L⁻¹ (Figure 8b), the molar adsorption capacity of Cd²⁺ (1.04 mmol g⁻¹, 117.0 mg g⁻¹) was visibly lower than that of Cu²⁺ (1.75 mmol g⁻¹, 112.4 mg g⁻¹), which indicated that the ion exchange was not the main mechanism during the heavy metals over MoS₂ NS. Similarly, Nguyen et al. also found that the ion exchange played a negligible role during the Cd²⁺ and Cu²⁺ adsorption over the activated carbon [43].

4. Conclusions

In summary, the ultrathin 2H-MoS₂ nanosheets with 1–2 layers were successfully obtained via a hybrid stagey with combination of quenching process and liquid-based exfoliation. The as-prepared 2H-MoS₂ nanosheets exhibited evident optical properties and could be accurately quantified with the absorbance at 615 nm in the range of 0.01–0.5 mg L⁻¹. Besides, the obtained 2H-MoS₂ nanosheets also showed a promising application in pollution control. It could be a candidate absorbent for the removal of dyes and heavy metals. This work provided an effective way for the large-scale fabrication of the two-dimensional nanosheets of transition metal dichalcogenides (TMDs) by liquid exfoliation.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/5/504/s1>, Figure S1. Linear fittings of dyes adsorption (a) and heavy metals (b and c) over bulk MoS₂ and MoS₂ NS with the Freundlich model, Table S1 Adsorption kinetics parameters of dyes and heavy metals adsorption over MoS₂ NS.

Author Contributions: S.H. and Y.L. (Yifan Liu) conceived the study, designed the experiments and wrote the manuscript. S.H., Z.Y. and Y.J. performed the experiments. F.Z. and K.L. finished the characterization and data analysis. Y.L. (Yuancai Lv) and X.C. edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Open Project Program of National Engineering Research Center for Environmental Photocatalysis (Grant No. 201904), Fuzhou University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kibsgaard, J.; Chen, Z.; Reinecke, B.N.; Jaramillo, T.F. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.* **2012**, *11*, 963–969. [[CrossRef](#)] [[PubMed](#)]
2. Oakes, L.; Carter, R.; Hanken, T.; Cohn, A.P.; Share, K.; Schmidt, B.; Pint, C.L. Interface strain in vertically stacked two-dimensional heterostructured carbon-MoS₂ nanosheets controls electrochemical reactivity. *Nat. Commun.* **2016**, *7*, 11796. [[CrossRef](#)] [[PubMed](#)]

3. Qiao, X.-Q.; Tian, F.-Y.; Hou, D.-F.; Hu, F.-C.; Li, D.-S. Equilibrium and kinetic studies on MB adsorption by ultrathin 2D MoS₂ nanosheets. *RSC Adv.* **2016**, *6*, 11631–11636. [[CrossRef](#)]
4. Ye, L.; Xu, H.; Zhang, D.; Chen, S. Synthesis of bilayer MoS₂ nanosheets by a facile hydrothermal method and their methyl orange adsorption capacity. *Mater. Res. Bull.* **2014**, *55*, 221–228. [[CrossRef](#)]
5. Lee, C.; Yan, H.; Brus, L.E.; Heinz, T.F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700. [[CrossRef](#)] [[PubMed](#)]
6. Zhang, Y.; Ye, J.; Matsuhashi, Y.; Iwasa, Y. Ambipolar MoS₂ Thin Flake Transistors. *Nano Lett.* **2012**, *12*, 1136–1140. [[CrossRef](#)]
7. Coleman, J.N.; Lotya, M.; O'Neill, A.; Bergin, S.D.; King, P.J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R.J.; et al. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **2011**, *331*, 568–571. [[CrossRef](#)]
8. O'Neill, A.; Khan, U.; Coleman, J.N. Preparation of High Concentration Dispersions of Exfoliated MoS₂ with Increased Flake Size. *Chem. Mater.* **2012**, *24*, 2414–2421. [[CrossRef](#)]
9. Tao, J.; Chai, J.W.; Lü, X.; Wong, L.M.; Wong, T.I.; Pan, J.; Xiong, Q.; Chi, D.; Wang, S. Growth of wafer-scale MoS₂ monolayer by magnetron sputtering. *Nanoscale* **2015**, *7*, 2497–2503. [[CrossRef](#)]
10. Motola, M.; Baudys, M.; Zazpe, R.; Krbal, M.; Michalicka, J.; Rodriguez-Pereira, J.; Pavlinak, D.; Prikryl, J.; Hromadko, L.; Sopha, H.I.; et al. 2D MoS₂ nanosheets on 1D anodic TiO₂ nanotube layers: An efficient co-catalyst for liquid and gas phase photocatalysis. *Nanoscale* **2019**, *11*, 23126–23131. [[CrossRef](#)] [[PubMed](#)]
11. Shen, J.; He, Y.; Wu, J.; Gao, C.; Keyshar, K.; Zhang, X.; Yang, Y.; Ye, M.; Vajtai, R.; Lou, J.; et al. Liquid Phase Exfoliation of Two-Dimensional Materials by Directly Probing and Matching Surface Tension Components. *Nano Lett.* **2015**, *15*, 5449–5454. [[CrossRef](#)] [[PubMed](#)]
12. Kim, J.; Kwon, S.; Cho, D.-H.; Kang, B.; Kwon, H.; Kim, Y.; Park, S.O.; Jung, G.Y.; Shin, E.; Kim, W.-G.; et al. Direct exfoliation and dispersion of two-dimensional materials in pure water via temperature control. *Nat. Commun.* **2015**, *6*, 8294. [[CrossRef](#)] [[PubMed](#)]
13. Dong, L.; Lin, S.; Yang, L.; Zhang, J.; Yang, C.; Yang, D.; Lu, H. Spontaneous exfoliation and tailoring of MoS₂ in mixed solvents. *Chem. Commun.* **2014**, *50*, 15936–15939. [[CrossRef](#)] [[PubMed](#)]
14. Zhou, K.-G.; Mao, N.-N.; Wang, H.; Peng, Y.; Zhang, H.-L. A Mixed-Solvent Strategy for Efficient Exfoliation of Inorganic Graphene Analogues. *Angew. Chem. Int. Ed.* **2011**, *50*, 10839–10842. [[CrossRef](#)] [[PubMed](#)]
15. Guardia, L.; Paredes, J.I.; Rozada, R.; Villar-Rodil, S.; Martinez-Alonso, A.; Tascón, J.D. Production of aqueous dispersions of inorganic graphene analogues by exfoliation and stabilization with non-ionic surfactants. *RSC Adv.* **2014**, *4*, 14115–14127. [[CrossRef](#)]
16. Smith, R.J.; King, P.J.; Lotya, M.; Wirtz, C.; Khan, U.; De, S.; O'Neill, A.; Duesberg, G.S.; Grunlan, J.C.; Moriarty, G.; et al. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. *Adv. Mater.* **2011**, *23*, 3944–3948. [[CrossRef](#)]
17. Zheng, J.; Zhang, H.; Dong, S.; Liu, Y.; Nai, C.T.; Shin, H.S.; Jeong, H.Y.; Liu, B.; Loh, K.P. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat. Commun.* **2014**, *5*, 2995. [[CrossRef](#)]
18. Zhuc, W.; Gao, X.; Li, Q.; Li, H.; Chao, Y.; Li, M.; Mahurin, S.M.; Li, H.; Zhu, H.; Dai, S. Controlled Gas Exfoliation of Boron Nitride into Few-Layered Nanosheets. *Angew. Chem. Int. Ed.* **2016**, *55*, 10766–10770. [[CrossRef](#)]
19. Jiang, B.; Tian, C.; Wang, L.; Xu, Y.; Wang, R.; Qiao, Y.; Ma, Y.; Fu, H. Facile fabrication of high quality graphene from expandable graphite: Simultaneous exfoliation and reduction. *Chem. Commun.* **2010**, *46*, 4920. [[CrossRef](#)]
20. Tang, Y.B.; Lee, C.-S.; Chen, Z.; Yuan, G.D.; Kang, Z.H.; Luo, L.B.; Song, H.S.; Liu, Y.; He, Z.; Zhang, W.; et al. High-Quality Graphenes via a Facile Quenching Method for Field-Effect Transistors. *Nano Lett.* **2009**, *9*, 1374–1377. [[CrossRef](#)]
21. Van Thanh, D.; Pan, C.-C.; Chu, C.-W.; Wei, K.-H. Production of few-layer MoS₂ nanosheets through exfoliation of liquid N₂-quenched bulk MoS₂. *RSC Adv.* **2014**, *4*, 15586–15589. [[CrossRef](#)]
22. Zhao, J.; Wang, Z.; Zhao, Q.; Xing, B. Adsorption of Phenanthrene on Multilayer Graphene as Affected by Surfactant and Exfoliation. *Environ. Sci. Technol.* **2013**, *48*, 331–339. [[CrossRef](#)] [[PubMed](#)]
23. Cao, Q.; Huang, F.; Zhuang, Z.; Lin, Z. A study of the potential application of nano-Mg(OH)₂ in adsorbing low concentrations of uranyl tricarbonate from water. *Nanoscale* **2012**, *4*, 2423. [[CrossRef](#)] [[PubMed](#)]

24. Zhang, D.-Q.; Chai, J.-X.; Jia, Y.-X.; Wang, L.-J.; Zhao, Z.-L.; Cao, M. Facile Preparation of Few-layer MoS₂-NS by Liquid-Phase Ultrasonic Exfoliation. In Proceedings of the 2017 International Conference on Manufacturing Engineering and Intelligent Materials (ICMEIM 2017), Guangzhou, China, 25–26 February 2017.
25. Hai, X.; Chang, K.; Pang, H.; Li, M.; Li, P.; Liu, H.; Shi, L.; Ye, J. Engineering the Edges of MoS₂ (WS₂) Crystals for Direct Exfoliation into Monolayers in Polar Micromolecular Solvents. *J. Am. Chem. Soc.* **2016**, *138*, 14962–14969. [[CrossRef](#)]
26. Ma, L.; Huang, G.; Chen, W.; Wang, Z.; Ye, J.; Li, H.; Chen, D.; Lee, J.Y. Cationic surfactant-assisted hydrothermal synthesis of few-layer molybdenum disulfide/graphene composites: Microstructure and electrochemical lithium storage. *J. Power Sources* **2014**, *264*, 262–271. [[CrossRef](#)]
27. Li, H.; Zhang, Q.; Yap, C.C.R.; Tay, B.K.; Edwin, T.H.T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390. [[CrossRef](#)]
28. Korn, T.; Heydrich, S.; Hirmer, M.; Schmutzler, J.; Schüller, C. Low-temperature photocarrier dynamics in monolayer MoS₂. *Appl. Phys. Lett.* **2011**, *99*, 102109. [[CrossRef](#)]
29. Chakraborty, B.; Matte, H.R.; Sood, A.K.; Ra, C.N.R. Layer-dependent resonant Raman scattering of a few layer MoS₂. *J. Raman Spectrosc.* **2013**, *44*, 92–96. [[CrossRef](#)]
30. Bagnall, A.; Liang, W.; Marseglia, E.; Welber, B. Raman studies of MoS₂ at high pressure. *Phys. B+C* **1980**, *99*, 343–346. [[CrossRef](#)]
31. Chou, S.S.; De, I.; Kim, J.; Byun, S.; Dykstra, C.; Yu, J.; Huang, J.; Dravid, V.P. Ligand Conjugation of Chemically Exfoliated MoS₂. *J. Am. Chem. Soc.* **2013**, *135*, 4584–4587. [[CrossRef](#)]
32. Wang, L.; Xu, Z.; Wang, W.; Bai, X. Atomic Mechanism of Dynamic Electrochemical Lithiation Processes of MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2014**, *136*, 6693–6697. [[CrossRef](#)]
33. Wilcoxon, J.P.; Newcomer, P.P.; Samara, G.A. Synthesis and optical properties of MoS₂ and isomorphous nanoclusters in the quantum confinement regime. *J. Appl. Phys.* **1997**, *81*, 7934–7944. [[CrossRef](#)]
34. Guan, G.; Zhang, S.; Liu, S.; Cai, Y.; Low, M.; Teng, C.P.; Phang, I.Y.; Cheng, Y.; Duei, K.L.; Srinivasan, B.M.; et al. Protein Induces Layer-by-Layer Exfoliation of Transition Metal Dichalcogenides. *J. Am. Chem. Soc.* **2015**, *137*, 6152–6155. [[CrossRef](#)] [[PubMed](#)]
35. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 1–4. [[CrossRef](#)] [[PubMed](#)]
36. Wu, P.; Yin, N.; Li, P.; Cheng, W.; Huang, M. The adsorption and diffusion behavior of noble metal adatoms (Pd, Pt, Cu, Ag and Au) on a MoS₂ monolayer: A first-principles study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 20713–20722. [[CrossRef](#)]
37. Zhan, W.; Jia, F.; Yuan, Y.; Liu, C.; Sun, K.; Yang, B.; Song, S. Controllable incorporation of oxygen in MoS₂ for efficient adsorption of Hg²⁺ in aqueous solutions. *J. Hazard. Mater.* **2020**, *384*, 121382. [[CrossRef](#)]
38. Lv, Y.; Zhang, R.; Zeng, S.; Liu, K.; Huang, S.; Liu, Y.; Xu, P.; Lin, C.; Cheng, Y.; Liu, M. Removal of p-arsanilic acid by an amino-functionalized indium-based metal–organic framework: Adsorption behavior and synergetic mechanism. *Chem. Eng. J.* **2018**, *339*, 359–368. [[CrossRef](#)]
39. Yang, H.; Yuan, H.; Hu, Q.; Liu, W.; Zhang, D. Synthesis of mesoporous C/MoS₂ for adsorption of methyl orange and photo-catalytic sterilization. *Appl. Surf. Sci.* **2020**, *504*, 144445. [[CrossRef](#)]
40. Luo, J.; Fu, K.; Sun, M.; Yin, K.; Wang, D.; Liu, X.; Crittenden, J.C. Phase-Mediated Heavy Metal Adsorption from Aqueous Solutions Using Two-Dimensional Layered MoS₂. *ACS Appl. Mater. Interfaces* **2019**, *11*, 38789–38797. [[CrossRef](#)]
41. Choi, M.; Jang, J. Heavy metal ion adsorption onto polypyrrole-impregnated porous carbon. *J. Colloid Interface Sci.* **2008**, *325*, 287–289. [[CrossRef](#)]
42. Li, H.; Xie, F.; Li, W.; Fahlman, B.D.; Chen, M.; Li, W. Preparation and adsorption capacity of porous MoS₂ nanosheets. *RSC Adv.* **2016**, *6*, 105222–105230. [[CrossRef](#)]
43. Nguyen, H.D.; Tran, H.N.; Chao, H.-P.; Lin, C.-C. Activated Carbons Derived from Teak Sawdust-Hydrochars for Efficient Removal of Methylene Blue, Copper, and Cadmium from Aqueous Solution. *Water* **2019**, *11*, 2581. [[CrossRef](#)]

44. Li, R.; Deng, H.; Zhang, X.; Wang, J.J.; Awasthi, M.K.; Wang, Q.; Xiao, R.; Zhou, B.; Du, J.; Zhang, Z. High-efficiency removal of Pb(II) and humate by a CeO₂–MoS₂ hybrid magnetic biochar. *Bioresour. Technol.* **2019**, *273*, 335–340. [[CrossRef](#)] [[PubMed](#)]
45. Yang, K.; Chen, B.; Zhu, X.; Xing, B. Aggregation, Adsorption, and Morphological Transformation of Graphene Oxide in Aqueous Solutions Containing Different Metal Cations. *Environ. Sci. Technol.* **2016**, *50*, 11066–11075. [[CrossRef](#)] [[PubMed](#)]
46. Wang, C.; Yang, R.; Wang, H. Synthesis of ZIF-8/Fly Ash Composite for Adsorption of Cu²⁺, Zn²⁺ and Ni²⁺ from Aqueous Solutions. *Materials* **2020**, *13*, 214. [[CrossRef](#)] [[PubMed](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).