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Hyper-Crosslinked Porous MoS₂-Cyclodextrin-Polymer Frameworks: Rapid and Durable Removal of Aromatic Phenolic Micropollutant from Water

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ABSTRACT

A reasonable and efficient strategy for the construction of hyper-crosslinked porous MoS_2 -CD-polymer frameworks (MoS_2CDPFs) was demonstrated. Here, MoS_2 nanosheets (NSs) can be decorated with amino functionalized β -Cyclodextrin, producing a nanoscale structural motif (MoS_2@CD) for the synthesis of MoS_2CDPFs. We demonstrated that CD polymer (CDP) as linker can be uniformly incorporated into the frameworks. Except for the pores created between MoS_2 NSs, polymer doping generates extra interspace between MoS_2 NSs and CD monomer. Interestingly, the resultant MoS_2CDPFs can rapidly sequester aromatic phenolic micropollutant bisphenol A (0.1 mM) from water with 93.2% adsorption capacity, which is higher than that of MoS_2, MoS_2@CD, and CDP. The intercalation between MoS_2 sheets with CDP imparts the frameworks durability in adsorption/desorption of aromatic phenolic micropollutants. Remarkably, the removal efficiency reduced only 3% after 10 regeneration-reuse cycles. These findings demonstrated that the porous

MoS₂-CD-polymer-based frameworks are promising adsorbents for rapid, flow-through water remediation.

TOC Graphic



Considerable concern has been raised over the industrial waste chemicals emitted in aqueous environmental system because prolonged exposure could adversely cause reproduction of wildlife and humans even in trace concentration. Representatively, Bisphenol A (BPA), a raw chemical material frequently used in industrial and residential applications, has estrogenic activity and is suspected of having endocrine disrupting activity.¹ Additionally, BPA is hardly degraded and easy bio-accumulate, making it urgent and important to develop a sustainable, effective, and economical removal method. Various technologies have been examined for BPA removal, such as gram-negative aerobic bacterium degradation, photocatalytical oxidation, enzyme-catalyzed reaction, oxidative removal, and adsorption method, etc.²⁻⁶ In addition, an emerging water purification technique, such as solar-driven steam generation, also certainly work for BPA polluted water.⁷⁻⁹ Especially, the adsorption methods are most widespread due to their cost-effective, ease of operation, and potential reusability. Nevertheless, the performance of removing BPA by adsorption

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method has been limited because of the low concentration of BPA in water sources and the associated difficulties in analysis.

So far, commercial activated carbon is one type of the most effectively and commonly used adsorbents for organic pollutants removal from water system.¹⁰ Slow pollutant uptake, energy intensive regenerating, and efficient difference on types inescapably hamper the activated carbons refined use in micropollutant remove.^{11,12} Several other novel adsorbents, such as Zr(IV)-based MOFs, multiwalled carbon nanotubes, and surfactant-modified zeolite, were emerged for removing BPA.¹³⁻¹⁵ However, the materials mentioned above were only tested in high concentration BPA aqueous solution (usually >0.5 mM), or the operations need long period time (more than 1 hour) for adsorption equilibrium. Therefore, it is desired to look for more superior strategy.

β-CD is a typical cyclic oligosaccharide natural product, which has hydrophobic core center and hydrophilic outer surface. Based on its host-gest recognition, β-CD is promising for adsorption.¹⁶ Typically, coupling molecules were used to string or polymerize β-CD monomer to form CD-polymer.¹⁷⁻¹⁹ Previous studies on CD-polymer mainly focus on non-rigid aromatic groups interacting CD.¹⁷ In contrast, pioneering work of Alsbaiee's in polymerization CD with coupling reagents containing active functional groups endowed rapid sequestration and high durability.¹⁸ However, low thermal stability of CD-polymer curtails its large-scale application. Loading CD on multifarious solid supports as stationary phase for benign separation was emerged as promising candidate.²⁰⁻²³ These strategies took advantage of both

building blocks, exhibiting enhanced versatility and stability. A typical method was developed by CD modification with Fe₃O₄ nanoparticles as the matrix for magnetic separation of BPA.²⁰ Two-dimensional (2D) nanomaterials, such as graphene oxide, C_3N_4 , and cellulose membrane,²¹⁻²³ were also used as substrates to be functionalized with CD. Because the lattice of molybdenum disulfide (MoS₂) is not matched with CD, few reports have been reported on the direct modification of MoS₂ with CD.²⁴ In addition, even though there have limited works on organic pollutants or mercury ions removal by MoS₂ based materials^{25, 26}, there is rarely relevant report on removing BPA.²⁷

MoS₂ nanosheets (NSs) have recently been venerated as the radiant stars among 2D materials because of their prominent mechanical and electrical properties.²⁸ Assembling pristine nanosheets into well-controlled three-dimensional (3D) hierarchical architectures will improve performance of materials, such as abundant porosity, large surface area, and good robustness *etc.*^{26, 29, 30} Up to now, diverse synthetic strategies for preparing MoS₂-based 3D frameworks have been developed.^{29,30} Especially, many efforts have been focused on polymer intercalation between MoS₂ sheets or growth and assembly MoS₂ on multi-dimensional polymers.³¹ Unfortunately, MoS₂ NSs have no functional groups, such as hydroxyl group and epoxy group in graphene oxide, for directly and effectively hybridizing with other building blocks. Thus, direct intercalation of MoS₂ NSs with polymer resulted in flocculation *via* van der Waals force is often found to be extremely insufficiently durable.



Figure 1. (a) Synthetic route and proposed formation mechanism of MoS_2CDPFs . Insert: the tawny powder is the final product MoS_2CDPFs . (b) The color change of the reaction system from dark to tawny.

Herein, we used aminated-CD modified MoS₂ NSs as a structural motif for the hyper-crosslinked MoS₂-CD-polymer construction of porous frameworks (MoS₂CDPFs). CD polymer acted as linker was uniformly incorporated into the hybrids. Besides the pores created between MoS₂ NSs, the introduction of polymerized CD produces extra gap between MoS₂ NS₅ and CD. With these merits, we used MoS₂CDPFs as enhanced adsorbents to remove BPA from water. Their rapid sequestration of micropollutant BPA (0.1 mM) from water combined with the highest removal efficiency far exceeded those of the single- and two-component hybrids. The intercalation between MoS₂ NSs with CD polymer imparts the frameworks durability in adsorption/desorption for aromatic phenolic micropollutants. As far as we know, this is the first example to integrate MoS₂ NSs and CD as a promising adsorbent for aromatic phenolic micropollutant removal from aqueous system.

Experimental Section

Materials. Tetrafluoroterephthalonitrile (TFTPN), n-butyllithium solution (1.6 M) and MoS_2 (99%) were purchased from Alfa Aesar. MoS_2 NSs were obtained by

chemical exfoliation method by a similar method according to the literature,³² and then dispersed in DMF as stock solution. K₂CO₃, p-Toluenesulfonyl chloride (p-TsCl), ethylenediamine (EDA), and β -CD were purchased from Tian Jin Med (China). Deionized H₂O was utilized throughout the studies. 22.8 mg of BPA was added into 1 L of H₂O, and then stirred at ambient condition for 24 h to form a clear stock solution (0.1 mM). The absorption peak position wavelength was characterized by UV-vis spectroscopy (λ_{max} , BPA = 276 nm) to detect the concentration.

Measurements. The samples were analyzed by FT-IR on a Nicolet FT-170SX spectrometer. The chemical composition of the samples was characterized by X-ray photoelectron spectroscopy (XPS, PHI-5702). X-ray powder diffraction (XRD) pattern was investigated on a Bruker AXS D8-Advanced diffractometer. Transmission electron microscope (TEM) images were recorded on TEM (JEOL, JEM-2100, 200kV). The Brunauer-Emmett-Teller (BET) surface area was tested by N₂ adsorption-desorption at 77 K with Micromeritics TriStar II 3020 analyzer. TGA test was heated to 600 °C under N₂ at a heating rate of 3 °C min⁻¹. ¹H-NMR spectrum was recorded on a JEOL ESC 400M instrument. UV-vis measurement experiment was recorded over the range 200–600 nm on a Hitachi U-3900.

Synthesis of Mono-6-deoxy-6-(*p*-tolylsulfonyl)- β -cyclodexhin (β -CD-oTs) and mono-6-deoxy-6-ethylenediamine- β -cyclodexhin (β -CD-EDA). β -CD-EDA was synthesized according to literature with little modification.²⁰ Typically, β -Cyclodextrin (3.0 g, 2.64 mmol) was suspended in water (25 mL), then NaOH (0.337 g, 8.2 mmol) in 1 mL of water was added over 3 min until the suspension became clarified.

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p-Toluenesulfonyl chloride (*p*-TsCl) (0.75 g, 3.96 mmol) in acetonitrile (1.5 mL) was added dropwise over 5 min, causing immediate formation of a white precipitate. After stirring at 25 0 C for 2 h, the pH was adjusted to ~ 6 using 1 M HCl. The reaction vessel was stored overnight at 4 0 C. The white precipitate was collected and recrystallized. The resulting product was afforded a pure white solid after vacuum drying for 12 h. mp: 179 $^{\circ}$ C; ¹H-NMR (400 MHz, DMSO-*d*): 7.75 (H-7, d, *J* = 8.4 Hz, 2 H), 7.43 (H-8, d, *J* = 8.4 Hz, 2 H), 5.67-5.72 (OH-2 and OH-3, m, 14 H), 4.85-4.83 (H-1, m, 7 H), 4.40 (OH-6, m, 6 H), 3.66-3.31 (H-2, H-3, H-4, H-5 and H-6, m, overlaps with HOD), 2.43 (H-9, s, 3 H) ppm; ESI-MS m/z: 1311.1725 [M + Na⁺].

β-CD-oTs (5.0 g, 3.9 mmol) was dissolved in EDA (5 mL, 75 mmol), and then reacted at 80°C for 4 h. The solution was removed by rotary evaporation after the reaction completed. The sediment was dissolved in methanol (3 mL) and precipitated with excess acetone three times. The white powder was dried at 25°C for 24 h. mp: 200 $^{\circ}$ C; ¹H-NMR (D₂O): 5.08 (d, H-1, 7H), 3.99-3.40 (H-2, H-3, H-4, H-5 and H-6, m, overlaps with HOD), 2.84 (H-8, 2H), 2.71 (H-9, 2H). ESI-MS m/z: 1177.1989 [M + H⁺].

Synthesis of β -cyclodextrin modified molybdenum(IV) sulfide (MoS₂@CD). MoS₂ NSs (180 mg) in DMF (50 mL) was sonicated for 2 h. 15 mL of DMF solution containing β -CD-EDA (360 mg, 0.3 mmol) was slowly added into above MoS₂ suspension. After sonicating and stirring overnight, MoS@CD was collected by centrifugation and washed several times with DMF/Diethyl ether. The product was dispersed in anhydrous DMF for direct use. Synthesis of Porous MoS₂CDPFs and β -Cyclodextrin-Polymer (CDP). For MoS₂CDPFs: TFTPN (0.412 g, 2.06 mmol), β -CD (0.400 g, 0.342 mmol), and K₂CO₃ (0.640 g, 4.63 mmol) was suspended in anhydrous DMF (20 mL). MoS₂@CD suspension (*x* mg in 5 mL anhydrous DMF) was added. The reaction was filled with N₂ for 5 min, stirred and sonicated for 1 h at r.t., and then stirred for 48 h at 85 °C. The solvent was removed, and the solid was re-suspended in iced H₂O (50 mL), then 1 M HCl was added dropwise until pH = 7. Solid was collected by centrifugation and wash with H₂O (3 × 10 mL), THF (5 × 10 mL), and CH₂Cl₂ (3 × 10 mL). The final tawny product was dried under vacuum for 24 h at r.t. For MoS₂CDPFs-1 ~ MoS₂CDPFs-4, different dosages of MoS₂@CD (*x* = 200 mg, 150 mg, 100 mg, 50 mg) were used. The MoS₂CDPFs-3 expressed the best removal efficiency for BPA hereinafter, so we focused on discussing this sample.

For CDP: CDP was synthesized as mentioned above except without adding MoS₂@CD suspension.

2.5. Batch adsorption studies. The batch adsorption test was performed at 25 °C. For the adsorption kinetic studies, sorbent powder (20 mg) was added into a vial, then H_2O (100 µL) was added and stand for 3 min. Pollutant stock solution (22.8 mg/L, 0.1 mM, 20 mL) was added and then stirred at 250 r.p.m.. 2 mL of the suspension was taken at specific time periods by syringe and filtered immediately. The pollutant concentration in filtrate was recorded by UV–vis spectroscopy.

For the regenerated/reused test, after each use, ethanol $(3 \times 5 \text{ mL})$ and deionized water $(3 \times 5 \text{ mL})$ were used to soak and rinse the adsorbent, and another cycle was conducted.

Results and discussion

Preparation and Characterization of MoS₂CDPFs. Figure 1 showed the structural evolution of MoS₂CDPFs from aminated-CD modified MoS₂, free CD, and linker TFTPN. Alsbaiee's pioneering work suggested that the porous CD polymer can be prepared by crosslinking CD with fluorinated rigid aromatic groups for rapid removal of phenol micropollutants from aqueous system.¹⁸ In order to obtain hyper-crosslinked MoS_2 based porous structure, we firstly modified MoS₂ NSs with aminated-CD as 2D building blocks, and then mixed with free CD and TFTPN in DMF for integration. What is worth mentioning, we deliberately fixed the molar ratio of TFTPN/CD at 6, in which the number of Ar-F (8.24 mmol) in TFTPN is higher than that of –OH (6.81 mmol) in CD. So, theoretical excrescent Ar-F can effectively link the –OH on MoS₂@CD sheets, rather than coupling with free CD. The uniform tawny color of the final product MoS_2CDPFs is very different from the pale yellow color of CDP without MoS_2 (Figure S1) suggesting that $MoS_2@CD$ sheets were well coupled with free CD by TFTPN linker.



Figure 2. Characterization of MoS₂CDPFs. (a) FTIR spectra of (i~vi) β -CD, TFTPN, MoS₂, MoS₂@CD, CDP, and MoS₂CDPFs-3; (b) XPS spectra of (i~v) MoS₂, CD-EDA, MoS₂@CD, CDP, and MoS₂CDPFs-3; (c, d) partial enlarged views of N1s in CD-EDA and MoS₂@CD, S2s and S2p in CDP and MoS₂CDPFs-3, respectively. (e) XRD spectra of (i~v) β -CD, MoS₂, MoS₂@CD, CDP, and MoS₂CDPFs-3.

The successful formation of the typical MoS₂CDPFs-3 was characterized by FT-IR spectrum. In Figure 2a, the final MoS₂CDPFs showed absorbance at 2242 cm⁻¹ belonging to the nitrile stretch, and the absorbance at 1470 cm⁻¹ belonging to C–C aromatic stretches. The C–F stretches resonated at 1268 cm⁻¹ were presented in the spectra of both CDP and MoS₂CDPFs-3 and displayed weaker compared to that of TFTPN, indicating partial -F substitution in CDP and MoS₂CDPFs-3.¹⁸ The O–H stretches at 3350 cm⁻¹ and aliphatic C–H stretches at 2930 cm⁻¹, which are typical absorbance of intact β -CD, were observed in CDP and MoS₂CDPFs-3.

XPS survey spectra revealed the evidence of bond formation. In Figure 2b, it was

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determined that C1s and O1s were two intensive elements in MoS₂CDPFs-3. Additional peaks at 693 eV, 395 eV, and 162 eV, which was attributed to F 1s, Mo3p, and S2p, respectively, were observed in MoS₂CDPFs-3 sample.³³ In Figure S3b, typical signals -CN (Ar) at 287.2 eV and C-F (Ar) at 284.4 eV in high-resolution XPS of C1s proved the crossliner role of TFTPN in CDP, which were also detected in Figure S6b for MoS₂CDPFs-3. In Figure S4, the existence of C-N both in C1s (285.7 eV) and N1s (~400.1 eV) revealed the aminated-CD establishment.³⁴ In Figure 2c, the XPS survey spectra revealed the evidence of aminated-CD modification on MoS₂ NSs. In N1s XPS spectrum, overlap between N1s and Mo3p was detected, and the dominant peak for Mo3p revealed that monolayer covered CD is very thin. However, only weak peaks of Mo3p were observed in MoS₂CDPFs-3 due to organic molecules intercalation (Figure S5 and S6). In addition to the N1s peak at 399.9 eV for C-N, N1s peak at 402.1 eV should ascribe to the coordination bond Mo-N between CD-EDA and MoS₂ monolayers.³⁴ In Figure 2d, additional peaks at 230 eV and 165 eV in MoS₂CDPFs-3 were attributed to S2s and S2p of MoS₂, respectively.^{33,34} Evidently, 2D structural motifs MoS₂@CD can be hyper-crosslinked with Ar-F on CDP, and will not influence the intrinsic polymerization of CD by TFTPN.



Figure 3. Typical TEM images of (a, b) MoS₂@CD, (c~e) MoS₂CDPFs-3, (f) (c) The typical EDX pattern of MoS₂CDPFs-3, and inset is the corresponding SAED pattern. (g) HAADF image and the corresponding STEM-EDS elemental mapping images of (h) carbon, (i) oxide, (j) nitrogen, (k) sulfur, (l, m) molybdenum in MoS₂CDPFs-3.

Further studies of XRD in Figure 2e revealed amorphous nature of CDP and $MoS_2CDPFs-3$ with a similar broad diffraction peak at 2θ of ~ 25° . The absence of characteristic diffraction peaks of CD is attributed to the lack of exact orientation in CD crystals.³⁵ However, the weak peaks at 2θ of 14.4, 32.7, 39.4, and 58.7° belong to the (002), (100), (006), and (110) reflection indexes of a hexagonal structure of MoS_2 (JCPDS no. 37-1492), which should attribute to the interspaced MoS_2 sheets.^{33,34}





Figure 4. (a) Nitrogen adsorption and desorption isotherms of CD, CDP, MoS₂@CD, and MoS₂CDPFs-3. (b) TGA curves of CDP, MoS₂@CD, and MoS₂CDPFs-3.

The structures of MoS₂CDPFs-3 were further confirmed by TEM images. Figure 3a and 3b showed that MoS₂@CD is stacked out of order. The attached CD can be hardly observed because of only molecular layer modification. In Figure 3c~3e, the formed MoS₂CDPFs-3 are assembled into ordered layered structure. SAED pattern in Figure 3f showed intrinsic amorphism, suggesting that no free CD and MoS₂ were survived. STEM-HAADF image and element mapping images ascertained that C, N, O, S and Mo were uniformly dispersed in MoS₂CDPFs-3 (Figure 3g~m). The morphology evolution of MoS₂CDPFs was collected in Figure S8. Notably, there is no visible pore in MoS₂CDPFs matrix, which is significantly different from the morphology of the amorphous CDP with submicron pore in Figure S8b. As the feed ratio of MoS₂@CD decreased, the MoS₂ NSs gradually became indistinct, and the overall structures became condensed. Remarkably, the morphology of MoS₂CDPFs-4 with lowest MoS₂ feeding is still quite different from that of pure CDP, demonstrating that MoS₂@CD

As shown in Figure 4a and S9, and Table S1, the N_2 adsorption–desorption isotherms and the pore size distribution profiles of MoS₂CDPFs showed type IV curve characteristic of mesoporous structures.³⁰ The BET surface area of MoS₂CDPFs-3 is 61.1116 m²g⁻¹, which is higher than that of the sum of CDP (12.0103 m²g⁻¹) and MoS₂@CD (15.4855 m²g⁻¹), indicating that MoS₂CDPFs-3 is not the simple physical mixture among the building blocks. Typically, the composition of MoS₂CDPFs-3 was also characterized by TGA. In Figure 4b, CDP had a sudden drop at ~280 °C, corresponding to a major weight loss about 91%. The weight loss about only 7% of the MoS₂@CD was ascribed to the loss of attached CD molecules. MoS₂CDPFs-3 expressed mild ~51% weight loss, indicating that the additional 44% of CDP was inserted between MoS₂ interlayers. The overall weight loss of MoS₂CDPFs-3 after heating to 600 °C is significantly lower than that of CDP, suggesting ~49% MoS₂ component.

Adsorption kinetics. In addition to the pores created between MoS₂ NSs, polymer doping generates extra interspace between MoS₂ NSs and CD monomer. With these merits, we tried to use MoS₂CDPFs as enhanced adsorbents to remove BPA from water. Batch adsorption kinetic studies were conducted in pure water (pH~7.0), in which un-deprotonated BPA was the main species.^{10,15} The sorption of BPA in the MoS₂CDPFs-3 as a function of contact time was shown in Figure 5a and 5b. The sorption of BPA in the MoS₂CDPFs-3 increased quickly as the contact time increased within 5 min, then increased slowly within the followed 15 min, and almost unchanged in the last 40 min. Notably, 83.6% of BPA was removed from the aqueous solution in the first 5 min. The adsorptions reached saturation to 92.1% by 30 min, and there was only 1.1% increased adsorption when the contact time was extended to

60 min. So we chose 30 min of contact time as the equilibration time for the subsequent tests. Additionally, MoS₂CDPFs-3 showed the highest adsorption capacity to BPA compared with that of MoS₂, MoS₂@CD, CDP, other MoS₂CDPFs samples, and the mixture of CDP and MoS₂ with the same components in MoS₂CDPFs-3 (Figure 5c, S10 ~ S11).



Figure 5. Adsorption kinetics of BPA by MoS₂CDPFs. (a) Effect of contact time of BPA pollution onto MoS₂CDPFs-3. (b) The corresponding time dependent absorbance of residual pollutant (black) and removal efficiency (blue) of BPA. (c) The absorbance of residual pollutant in adsorption equilibrium state (black) and the removal efficiency (blue) of the samples by different adsorbents. (d) Pseudo-second-order kinetic plots (black) and pseudo-first-order kinetic plots (blue) of BPA. The adsorption of BPA is better modeled with second-order kinetics than first-order kinetics.

The rate of adsorption process was further analyzed by kinetic study. To analyze the kinetics of BPA sorption in the MoS₂CDPFs-3, pseudo-first-order rate equation and pseudo-second-order rate equation were used to simulate the kinetic sorption in Figure 5d, and the relative parameters were recorded in Table S2. The correlation coefficient for the linear plots in pseudo-second-order equation is closer to 1 ($R^2 = 0.9999$), which is more accurate than that in pseudo-first-order equation ($R^2 = 0.9373$). So we described the kinetic sorption by the pseudo-second-order rate model. The equilibrium sorption capacity of BPA in MoS₂CDPFs-3 was calculated from the slope in 21.51 mg/g. Pseudo-second-order rate equation is based on the assumption that the rate-limiting step is a chemical process in which valence forces are shared or exchanged of electrons between adsorbents and adsorbates.³⁷ The fast sorption of BPA by MoS₂CDPFs-3 in the pseudo-second-order rate model indicate that the main sorption of BPA in the MoS₂CDPFs-3 is chemical sorption or surface complexation rather than physical adsorption.³⁷



Figure 6. (a) Effect of solid content on BPA sorption to MoS₂CDPFs-3 at 25 °C. (b) Sorption isotherms of BPA on MoS₂CDPFs-3 at 25 °C. The solid blue line is Langmuir model simulation, the dashed red line is Freundlich model simulation, and the points represent experimental data.

Effect of solid content and adsorption isotherms. To evaluate the removal capacity,

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the feeding adsorbent should be considered in practical application process. As shown in Figure 6a, when we fixed the pollutant concentration at 22.8 mg/L and increased the adsorbent dosages from 0.2 g/L to 1.8 g/L, the adsorption efficiency increased from ~40.0 % to ~93.5%, and then remained consistently. According to the distribution coefficient K_d , it is clear that the K_d values are independent of adsorbent contents, disclosing that K_d values will not decrease as the increase of adsorbent at low contents.³⁸

As shown in Figure 6b, Langmuir and Freundlich isotherm models were further used to quantify the sorption data to better understand the sorption mechanism.³⁹ The relative parameters calculated were showed in Figure S12 and Table S3. The correlation coefficient for the linear plots in Langmuir model is closer to 1 ($R^2 =$ 0.9915), which is more accurate than that of Freundlich model ($R^2 = 0.8229$), suggesting that the sorption isotherm is better simulated by the Langmuir model. Considering aminated-CD firstly grafted on the surface of MoS₂, extra interspace between MoS₂ NSs and CD were generated as the pores created among CD, and the pores were dispersed homogeneously in the whole materials. So we can state that BPA is monolayer adsorption on the surface of MoS₂CDPFs-3 with a finite number of identical sites. In addition, according to the theoretical calculation in Langmuir model, we found that the C_{s, max} value is 50.25 mg/g at room temperature and neutral condition. Moreover, MoS₂CDPFs-3 has better efficiency than other adsorbents previously reported (Table S4).

Reusability. The sorption-desorption reusability of sorbent for aromatic BPA is a

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crucial factor in real long-term performance work. After sorption, the BPA desorption was performed by washing with alcohol and water. After dried at room temperature, the recycled MoS₂CDPFs-3 sample was reused. As shown in Figure 7a, the removal efficiency of MoS₂CDPFs-3 decreased slightly from 93.2% to 90.1% after 10 cycles of regeneration/reuse experiments. It indicated that MoS₂CDPFs are promising candidate for the durable removal of BPA from aqueous solutions with good chemical stability and reusability. The MoS₂CDPFs-3 after 10 time cycles has little morphology change in Figure 7b, further confirming the stability and reusability of the MoS₂CDPFs-3.



Figure 7. (a) The average removal efficiency of BPA by MoS₂CDPFs-3 after consecutive regeneration cycles. (b) Typical TEM image of reused MoS₂CDPFs-3 after 10 time cycles.

Conclusions

In conclusion, we firstly functionalized MoS₂ NSs by aminated-CD as nanoscale structural motif, and then constructed hyper-crosslinked porous MoS₂CDPFs by integration with TFTPN and free CD monomers. We demonstrated that CD polymer as linker can uniformly incorporate into hybrids. Except for the pores created between MoS₂ NSs, polymer doping generates extra interspace between MoS₂ NSs and CD

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monomer. Interestingly, MoS₂CDPFs-3 rapidly retain aromatic phenolic micropollutant BPA (0.1 mM) from water with 93.2% adsorption capacity, which is higher than that of MoS₂, monolayer CD decorated MoS₂, CDP, and the mixture of CDP and MoS₂. The BPA sequestration by MoS₂CDPFs-3 was better simulated by pseudo-second-order rate model kinetic sorption and the Langmuir model sorption isotherm. The intercalation of MoS₂ sheets with CD polymer imparts the frameworks durability in adsorption/desorption for aromatic phenolic micropollutants. Remarkably, the removal efficiency was reduced only 3.1% after 10 regeneration-reuse cycles. These findings indicate that hyper-crosslinked porous MoS₂CDPFs-3 serve as a promising adsorbent for aromatic phenolic micropollutant removal from water.

ASSOCIATED CONTENT

Supporting Information

Characterizations, Supporting Figures and Tables are available free of charge via the Internet at http://pubs.acs.org.

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