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Supporting Information

Polyoxometalate@MIL-101/MoS$_2$: a composite material based on MIL-101 platform with enhanced performances

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S-1. Synthetic methods
S-1.1 Synthesis of MIL-101.
MIL-101 was synthesized according to the method reported previously.$^{31}$ In brief, a mixture containing Cr(NO$_3$)$_3$·9H$_2$O (0.40 g, 1.00 mmol), 1,4-benzenedicarboxylic acid (0.16 g, 0.96 mmol), hydrofluoric acid (1 mmol), and water (4.80 mL) was sealed in a Teflon autoclave and heated at 220 °C for 8 h. The product was washed by DMF and ethanol for several times and dried at 80 °C.

S-1.2 Synthesis of PW$_{11}$Fe@MIL-101.
This preparation process of PW$_{11}$Fe@MIL-101 is similar to that of PW$_{11}$Fe@MIL-101/MoS$_2$, except that MIL-101 was used for replacing MIL-101/MoS$_2$.

S-2. Dye adsorption experiments
S-2.1 experiments
The adsorbents were dried under vacuum at 120 °C for 12h and then kept in a desiccator before the adsorption experiments. Taking the RhB adsorption experiments for example, the RhB aqueous solutions were prepared by dissolving solid RhB in ultrapure water. The adsorption experiments were performed under ambient conditions (298 ± 2 K) in the aqueous solutions. In a typical process, 100 mL of the RhB solution was stirred continually by a magnetic bar in the dark, and the adsorption test was started when 20 mg of the adsorbent was added. At per-determined time intervals, the supernatant was taken and analyzed using a UV-Vis spectrophotometer at the wavelength of 554 nm. During the adsorption kinetic experiments, the RhB solutions with the concentrations of 50, 100, and 200 mg L$^{-1}$, respectively, were used. In the adsorption thermal isotherm studies, the concentrations of RhB varied from 50 to 400 mg L$^{-1}$.

The amount of adsorbed dye at equilibrium, $q_e$ (mg g$^{-1}$), was calculated using the following equation:

$$q_e = \frac{(C_0-C_e)\times V}{W}$$  \hspace{1cm} (1)

where $C_0$ (mg L$^{-1}$) and $C_e$ (mg L$^{-1}$) mean the initial and equilibrium concentrations of RhB, respectively. $V$ (L) and $W$ (g) mean the volume of the RhB solution and the weight of the
adsorbent, respectively.

5.2.2 Adsorption kinetics.
The adsorption kinetics of RhB on the adsorbents were studied using two common models: pseudo-first-order, pseudo-second-order:

Pseudo-first-order equation:

\[ \ln(q_e - q_t) = \ln q_e - \frac{K_1}{2.303} t \]  \hspace{1cm} (2)

where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the adsorption capacities at equilibrium and time \( t \) (min), respectively. \( K_1 \) (g mg\(^{-1}\) min\(^{-1}\)) is the kinetic rate constant.

Pseudo-second-order kinetic equation:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm} (3)

where \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the second-order rate constant.

5.2.3 Adsorption thermodynamic.
Two most frequently used isotherm models were selected to fit the data of adsorption experiments, which are Langmuir and Freundlich isotherm models. They were expressed in the following equation.

The Langmuir isotherm equation:

\[ \frac{1}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \]  \hspace{1cm} (5)

Where \( K_L \) (L mg\(^{-1}\)) is Langmuir constant, \( q_m \) (mg g\(^{-1}\)) is the maximum adsorption capacity.

Freundlich equation:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  \hspace{1cm} (6)

where \( K_F \) and \( n \) are Freundlich constants.\(^{52} \)

5.2.4 Regeneration and reuse of PW\(_{11}\)Fe@MIL-101/MoS\(_2\).
The used adsorbent was recovered from the RhB aqueous solution by centrifugation. Before the adsorbent was reused, it was repeatedly washed with the aqueous solution of NaCl and DMF. This method was reported in previous paper.\(^{53} \) After the adsorbent was immersed in the NaCl aqueous solution, RhB cations could be partially removed through the cation-exchange process. Moreover, RhB could be further removed after the sample was washed with DMF because of the high solubility of RhB in DMF. The detailed desorption processes can be described as follows. The used PW\(_{11}\)Fe@MIL-101/MoS\(_2\) sample was dispersed in the aqueous solution of NaCl (0.5 M) and stirred for tens of mins. Then, it was separated, dispersed in DMF, and further stirred for another tens of mins. As shown Fig. S12, RhB could be effectively removed from the adsorbent through being treated in the NaCl aqueous solution and DMF, respectively. These processes were carried out repeatedly until no adsorption peaks of RhB were observed in the UV-vis spectra, which indicates that the removable RhB molecules have been fully desorbed from the adsorbent. Finally, the adsorbent was washed with ethanol to remove DMF from the sample. The regenerated sample was dried overnight at 393 K under vacuum before it was reused for the next adsorption experiments.
Fig. S1. The structures of a) RhB and b) MO.

Fig. S2. The structural images of PW_{12}Fe.

Fig. S3. The XRD patterns of (a) MoS_{2} synthesized using Na_{2}MoO_{4} and C_{2}H_{5}NS as the reactants, (b) the sample obtained through treating MIL-101 in the solution containing Na_{2}MoO_{4} and C_{2}H_{5}NS under microwave irradiation, and (c) MIL-101.
Fig. S4. Image of the samples of MIL-101/MoS$_2$ (left) and MIL-101 (right).

Fig. S5. The adsorption capacities of RhB over MIL-101/MoS$_2$ samples synthesized with different reaction time.

Fig. S6. EDS spectrum of MIL-101/MoS$_2$. During the process of EDS analysis, the sample was dispersed on the Cu-Zn alloy.
Fig. S7. EDS spectrum of PW11Fe@MIL-101/MoS2.

Fig. S8. The TG curve of PW11Fe@MIL-101/MoS2.

<table>
<thead>
<tr>
<th>$c_0$ (mg L$^{-1}$)</th>
<th>$q_{e,exp}$ (mg g$^{-1}$)</th>
<th>Pseudo-first-order kinetic</th>
<th>Pseudo-second-order kinetic</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{e,cal}$ (mg g$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>50</td>
<td>140.81</td>
<td>44.22</td>
<td>0.9841</td>
</tr>
<tr>
<td>100</td>
<td>236.39</td>
<td>53.22</td>
<td>0.8858</td>
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<tr>
<td>200</td>
<td>355.83</td>
<td>105.56</td>
<td>0.9521</td>
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</table>
Table S2. Comparison for the removal of RhB by various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg g(^{-1}))</th>
<th>Reusability</th>
<th>Ref.</th>
</tr>
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<tr>
<td>MIL-68(Al)</td>
<td>1111.11(^a)</td>
<td>Yes</td>
<td>S4</td>
</tr>
<tr>
<td>[H(_2)N(Me)](_2)]<a href="DMF">Ln(_3)(OH)(bpt)(_3)(H(_2)O)(_3)</a>(_2):(H(_2)O)(_4)</td>
<td>735(^b)</td>
<td>No report</td>
<td>S5</td>
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<tr>
<td>PW(_{11})Fe@MIL-101/MoS(_2)</td>
<td>560(^c)</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>MIL-101/MoS(_2)</td>
<td>500 (^a)</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>MoS(_2)/MIL-101</td>
<td>344.8 (^a)</td>
<td>Yes</td>
<td>S6</td>
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<tr>
<td>MIL-68(In)-NH(_2)/graphite oxide composite</td>
<td>267 (^a)</td>
<td>Yes</td>
<td>S7</td>
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<tr>
<td>Ni doped FeO(OH)-NWs-AC</td>
<td>210.17 (^a)</td>
<td>No report</td>
<td>S8</td>
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<tr>
<td>Zn(phenDIB)(AOBTC)(_{0.5})</td>
<td>127.5 (^a)</td>
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<td>S9</td>
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<tr>
<td>Graphene oxide</td>
<td>154.8 (^a)</td>
<td>No report</td>
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<td>Graphene oxide/Beta zeolite composite</td>
<td>64.47 (^a)</td>
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<td>S11</td>
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<tr>
<td>MIL-125(Ti)</td>
<td>59.92 (^a)</td>
<td>No report</td>
<td>S12</td>
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<td>Sodium montmorillonite</td>
<td>42.19 (^a)</td>
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<td>S13</td>
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<td>Reduced Graphene oxide/ZnO</td>
<td>32.6 (^a)</td>
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<td>S14</td>
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<td>Beta Zeolite</td>
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<td>Zeolite</td>
<td>13.22 (^a)</td>
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<td>S15</td>
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<td>MCM-22</td>
<td>0.054 (^a)</td>
<td>No report</td>
<td>S16</td>
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</table>

\(^a\). maximum adsorption capacity; b. RhB concentration, 300 mg L\(^{-1}\); c. RhB concentration, 400 mg L\(^{-1}\).

Table S3. Kinetic model parameters of RhB adsorption onto PW\(_{11}\)Fe@MIL-101/MoS\(_2\).

<table>
<thead>
<tr>
<th>(c_0) (mg L(^{-1}))</th>
<th>(q_{e,exp}) (mg g(^{-1}))</th>
<th>(q_{e,cal}) (mg g(^{-1}))</th>
<th>(R^2)</th>
<th>(q_{e,cal}) (mg g(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>186.23</td>
<td>38.68</td>
<td>0.9361</td>
<td>188.68</td>
<td>0.9999</td>
</tr>
<tr>
<td>100</td>
<td>373.34</td>
<td>105.80</td>
<td>0.9811</td>
<td>384.62</td>
<td>0.9999</td>
</tr>
<tr>
<td>200</td>
<td>520.25</td>
<td>121.73</td>
<td>0.9397</td>
<td>526.32</td>
<td>0.9998</td>
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</tbody>
</table>

Fig. S9. XRD of as-synthesized sample (upper) and regenerated sample (lower) of PW\(_{11}\)Fe@MIL-101/MoS\(_2\).
Fig. S10. The reusability of PW$_{11}$Fe@MIL-101/MoS$_2$ for removal of RhB.

Fig. S11. Plots of pseudo-second-order kinetics of MO adsorption over MIL-101, PW$_{11}$Fe@MIL-101, MIL-101/MoS$_2$, and PW$_{11}$Fe@MIL-101/MoS$_2$ (MO, 200 mg L$^{-1}$; adsorbents, 0.2 g L$^{-1}$).

Fig. S12. The UV-vis spectra of filtrates ((a) NaCl aqueous solution and (b) DMF) used in the desorption processes of RhB from PW$_{11}$Fe@MIL-101/MoS$_2$.

References
S4 M. S. Tehrani, R. Zare-Dorabei, RSC Adv., 2016, 6, 27416-27425.