Integration of Phosphotungstic Acid into Zeolitic Imidazole Framework-67 for Efficient Methylene Blue Adsorption

Shang Wei, Jiayi Wu, Peng Chen, Bo Fu, Xinbao Zhu, and Muhua Chen*

ABSTRACT: To enhance the dye adsorption capacity of zeolitic imidazolate framework-67 (ZIF-67), phosphotungstic acid (HPW) was integrated into ZIF-67 to prepare composite adsorbents. Characterization results demonstrated that the electronegative HPW was uniformly and tightly deposited on the electropositive ZIF-67. Methylene blue (MB) was selected as a model contaminant to evaluate the adsorption performance of hybrid adsorbents. Results showed that HPW@ZIF-67 had excellent adsorption capacity toward cationic MB. The optimal ZIF-67-0.2 HPW sample with a HPW dosage of 9.9 wt % presented an adsorption capacity of 446.4 mg g\(^{-1}\). ZIF-67-0.2 HPW displayed good reusability, and the adsorption data can be well described by pseudo-second order and Langmuir isotherm models. The adsorption mechanism was ascribed to the preferred electrostatic attraction and π−π stacking between MB and composite adsorbents. This work provides a route to enhance organic dye removal efficiency of ZIF materials through regulation of surface charge property and sheds light on the development of ZIF-based adsorbents.

INTRODUCTION

Industrialization activities have led to increasing amounts of water contaminants into the global water system.\(^1\) In particular, organics dyes with extensive applications are discharged from a wide range of industries including textiles, paper, plastics, and paints.\(^2\) Dye-contaminated wastewater without proper treatment would lead to serious damage to the environment and human health.\(^3\) Diverse methods have been proposed for dye removal, for instance, adsorption, oxidation, electrochemical process, membrane filtration, photolysis, and precipitation.\(^4,5\) Adsorption is regarded as an efficient and economic technique because of its convenient operation and reduced impacts on the environment.\(^6\) To date, various adsorbents including zeolite, carbon, polymers, metal organic frameworks (MOFs), and zeolitic imidazole frameworks (ZIFs) have proven to be effective for dye removal.\(^7\) Among them, ZIFs outperform other materials due to their ultrahigh surface area, tunable porosity, and easy modification.\(^8\)

ZIF-67 is a kind of ZIF material that is formed by Co\(^{2+}\) center and 2-methylimidazole ligand.\(^9\) ZIF-67 exhibits abundant porosity and large surface area, and its topology structure is feasible for post modification.\(^10,11\) Prior studies have successfully applied ZIF-67 for organic pollutant removal. For instance, Xue et al.\(^12\) synthesized magnetic ZIF-67 and used it for the selective adsorption of binary anionic Direct Blue 86 from mixed dye solution and achieved a desirable selectivity. They found that proper modification of ZIF-67 surface can improve the cationic dye adsorption on ZIF-67. Nazir et al.\(^13\) also confirmed that the adsorption capacity of CoAl-LDH modified with ZIF-67 for methylene blue (MB) could reach 57.2 mg g\(^{-1}\). However, the surface modification of ZIF-67 still faces the challenges of complicated procedures, toxic reagents, and limited adsorption capacity. There is a need to develop a facile surface modification approach to enhance the adsorption performance of ZIF-67.

Phosphotungstic acid (HPW) is a typical polyoxometalate with nontoxic nature, oxo-enriched surface, and strong electro-
negative.\textsuperscript{14,15} It has been widely applied in the fields of catalysis, electrochemistry, and medicine. HPW with a negative potential holds great potential to remove cationic organic dyes.\textsuperscript{16–18} However, the low surface area and poor porosity restricts its practical application.\textsuperscript{19} Also, the high solubility of HPW in aqueous media reduces its reusability and recyclability as an adsorbent.\textsuperscript{14} To address these problems, many materials have been investigated as suitable carriers/substrates for HPW.\textsuperscript{19} Considering that ZIF-67 is abundant in micropores and has multiple coordination sites and positive in charge, it might be suitable for HPW immobilization. Moreover, the multiple coordination sites make it an excellent support for HPW.\textsuperscript{20}

Herein, HPW-modified ZIF-67 (ZIF-67-\textit{n} HPW) was prepared in a facile way. The charge interactions of ZIF-67 and HPW endowed the composite with high affinity and compatibility. The adsorption capacity was tested with cationic MB. Moreover, the impacts of different parameters, adsorption isotherms, kinetics, and adsorption mechanisms were investigated. Results showed that such adsorbents exhibited superior adsorption ability for the cationic dye.

\section*{EXPERIMENTAL SECTION}

Materials. Co(NO$_3$)$_2$·6H$_2$O (99\%) and HPW were obtained from Macklin. 2-Methylimidazole (98\%) was purchased from Tianjin Chemical Reagent Research Institute and methanol (99.5\%) was purchased from Nanjing Reagent Co., Ltd. All reagents were used without further purification.

Preparation of Adsorbents. ZIF-67 was synthesized according to a previous report.\textsuperscript{21} Typically, 1.164 g of Co(NO$_3$)$_2$·6H$_2$O and 0.657 g of 2-methylimidazole were dispersed in 50 mL methanol separately. The abovementioned solutions were mixed by magnetic stirring for 3 h and aged for 24 h at 25 $^\circ$C. The obtained ZIF-67 was gathered using filtration, and then moved into an oven at 70 $^\circ$C for 8 h.

For synthesizing ZIF-67-$n$ HPW, different weights of HPW (0.05, 0.2, 0.4 g) were dissolved into 2-methylimidazole methanol solution and then treated with ultrasound for 20 min. The following procedures were the same as for the preparation of ZIF-67. HPW-modified ZIF-67 was marked as ZIF-67-$n$ HPW ($n = 0.05, 0.2, 0.4$).

Characterization. XRD patterns of all samples were obtained using a Rigaku Ultima IV, operated at 40 kV at a range of 3–50$^\circ$ with Cu Ka radiation. FTIR spectra were collected using a Thermo Electron Nicolet-6700 spectrometer with samples dispersed in KBr. The isotherms of nitrogen adsorption–desorption were measured with a JW-BK132 instrument. SEM images and the EDS spectra were taken using a JSM-7600F scanning electron microscope. Zeta potentials were determined using a Malvern Zetasizer Nano-ZS. The pH values of solutions were measured using a PHS-25 pH meter.

Adsorption Studies. The adsorption properties were investigated using 50 mg L$^{-1}$ MB as a model dye at room temperature, and the ratio of mass of the absorbent to the volume of MB solution was 1:4 (20 mg of ZIPF-67-0.2 HPW was added to 80 mL MB solution with a pH of 6.5). At a given time, the filtered liquid was collected through 0.22 $\mu$m filter (fully adsorbing MB) and measured at 665 nm using a Unico UV-2802 spectrophotometer. As for the removal percentage ($R$), adsorption capacity, and equilibrium adsorption capacity ($q_0$, $q_e$: mg g$^{-1}$) of the absorbent were determined using the following equations

\begin{equation}
R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
\end{equation}

\begin{equation}
q_t = \frac{(C_0 - C_t) \times V}{m} \tag{2}
\end{equation}

\begin{equation}
q_e = \frac{(C_0 - C_e) \times V}{m} \tag{3}
\end{equation}

where $C_0$, $C_t$, and $C_e$ (mg L$^{-1}$) are dye concentrations at the beginning, at a given time, and at equilibrium, respectively. $V$ (mL) and $m$ (mg) represents the dye solution volume and absorbent mass, respectively.

Detailed adsorption experiments were conducted on the optimum absorbent. The influence of initial pH (adjusted by 0.1 M NaOH and HCl) from 3.0 to 11.0 and coexisting ions on adsorption was explored, and 20 mg of ZIF-67-0.2 HPW was added to 80 mL 50 mg L$^{-1}$ MB solution. After stirring for 2 h to reach adsorption equilibrium, the solution concentrations were measured using a UV spectrophotometer, and the adsorption capacity was calculated to study the interference of pH values on adsorption. The adsorption isotherms were conducted with initial MB concentrations (pH = 6.5, 20 mg of
ZIF-67-0.2 HPW added to 80 mL MB solution and stirred for 2 h) changing from 50 to 400 mg L\(^{-1}\), and adsorption thermodynamics were analyzed at different temperatures (15, 25, and 35 °C, 20 mg of ZIF-67-0.2 HPW added to 80 mL MB solution with pH = 6.5 and stirred). The reusable experiments of ZIF-67-0.2 HPW were performed at 25 °C (pH = 6.5) for eight cycles. During the experiments, the adsorbent was desorbed by stirring with ethanol for 30 min, filtered and collected, and desorption was repeated three times.

## RESULTS AND DISCUSSION

### Structure and Morphology Analysis.

XRD was used to study the crystal structures and confirm the successful synthesis of adsorbents. Figure 1a compares XRD patterns of ZIF-67 and ZIF-67-n HPW. Some existing diffraction peaks \([7.4° (011), 10.4° (002), 14.7° (022)]\) of the synthesized ZIF-67 matched well with the peaks of ZIF-67 reported in a previous work.\(^{22,23}\)

This confirmed the successful synthesis of ZIF-67. The characteristic peaks of ZIF-67 can also be observed in ZIF-67-n HPW composites. It indicated that the HPW modification process had no significant influence on the crystalline structure of ZIF-67. The peaks located at 6.8° (010), 15.9° (220), and 19.2° (321) of HPW slightly moved to higher angles in ZIF-67-n HPW \((n = 0.2, 0.4)\).\(^{25}\)

Due to the uniform distribution, no characteristic diffraction peaks of HPW were found in ZIF-67-0.05 HPW.

FTIR spectra were investigated to characterize the functional groups of adsorbents and are presented in Figure 1b. The stretch absorption peaks to band vibration were 1080 cm\(^{-1}\) and 755 cm\(^{-1}\) for P=O and N band of HPW \((\text{W} = 0.05, 0.2, 0.4)\) all achieved higher adsorption capacity of MB than ZIF-67, which were 112.1, 198.9, and 199.1 mg g\(^{-1}\), respectively. Considering the HPW dosage, ZIF-67-0.2 HPW is regarded as the optimal adsorbent.

### Adsorption Performance.

Figure 3a shows the effects of contact time on the adsorption process. The adsorption capacities of ZIF-67-n HPW \((n = 0.2, 0.4)\) increased quickly within the initial 5 min and came to an equilibrium with no considerable change over the rest of the time. Moreover, it took more time for ZIF-67-0.05 HPW and ZIF-67 to reach the adsorption plateau. After 1 h, ZIF-67-n HPW \((n = 0.05, 0.2, 0.4)\) achieved higher adsorption capacity of MB than ZIF-67, which were 112.1, 198.9, and 199.1 mg g\(^{-1}\), respectively. Considering the HPW dosage, ZIF-67-0.2 HPW is regarded as the optimal adsorbent.

The impacts of initial concentrations were examined. Figure 3b indicates that the adsorbed MB on ZIF-67-0.2 HPW increased from 199.2 mg g\(^{-1}\) to a higher level and then increased slowly. Besides, the removal efficiency was 99.6% in the beginning and then decreased as the initial MB concentration increased. It could be explained that MB was easier to be adsorbed on adsorbent active sites with higher initial concentration. However, it would become hard for the adsorbent to capture more MB molecules under high concentrations. When the active sites were occupied sufficiently, the adsorption would be saturated and then the adsorption capacity reached a maximum level.

Kinetics of MB adsorption were conducted at 25 °C. After equilibriums were reached, pseudo-first order (PFO) and pseudo-second order (PSO) model were adopted to fit the experimental data. These two kinetic equations are expressed by

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]

where \(q_e\) and \(q_t\) (mg L\(^{-1}\)) are adsorption capacities at equilibrium and time \(t\) (min), respectively, and \(k_1\) (min\(^{-1}\)) and \(k_2\) (g (mg min\(^{-1}\))\(^{-1}\)) are the constants of PFO and PSO equations, respectively.

The linear regression results of PFO and PSO are presented in Figure 4 and Table S1. The fitted PSO model well described the data of MB adsorbed onto ZIF-67-0.2 HPW and possessed higher \(R^2\) (0.9995) compared with the PFO model \((R^2 = 0.6550)\). The PSO model implied that the adsorption sites and chemisorption were the main controlling factors during MB adsorption.

### Table 1: Textural Properties of Prepared Adsorbents

| adsorbent | \(S_{BET}/\text{m}^2\cdot\text{g}^{-1}\) | \(V_{pore}/\text{cm}^3\cdot\text{g}^{-1}\) | average pore size/\(\text{nm}\) |
|-----------|----------------|----------------|------------------|
| ZIF-67    | 1285.60        | 0.708          | 2.204            |
| ZIF-67-0.05 HPW | 532.62        | 0.388          | 2.912            |
| ZIF-67-0.2 HPW | 14.09          | 0.074          | 20.877           |
| ZIF-67-0.4 HPW | 7.21           | 0.047          | 25.848           |

became smaller and the rhombic dodecahedral turned into an irregular shape. The morphology transformation of ZIF-67 matched the analysis of BET. Smaller sizes of adsorbents may expose more adsorption sites for the improvement of MB adsorption.\(^{32}\)

Furthermore, the EDS spectra of ZIF-67 and ZIF-67-0.2 HPW are shown in Figure 2e,f to analyze the existing elements. The result of ZIF-67-0.2 HPW indicated that it contained W element from HPW during the synthesis process compared to bare ZIF-67 and the blue dots representing W element were uniformly distributed in the EDS mapping, which clearly illustrated the existence and well dispersion of HPW in the composite.

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The adsorbate–adsorbent interactions were discussed using the Langmuir and Freundlich models.38 It is presumed that the single layer adsorption process happens on adsorbents with no chemical reaction between adsorbate species by the Langmuir model (eq 6). On the contrary, the Freundlich model (eq 7) posits adsorption occurs on the surface of adsorbent and adsorbate molecule can interact.39 Moreover, an equilibrium parameter $R_L$ (eq 8) was adopted to figure out if the adsorption was favorable or not.40 Employed adsorption models are described by

$$\frac{C_e}{q_t} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$$  \hspace{1cm} (6)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (7)

Figure 2. SEM images of ZIF-67 (a), ZIF-67-n HPW [$n = 0.05$ (b), 0.2 (c), and 0.4 (d)], EDS spectra of ZIF-67 (e), and ZIF-67-0.2 HPW (f).
where $q_{\text{max}}$ (mg g$^{-1}$) and $C_e$ (mg L$^{-1}$) are the maximum adsorption capacities and equilibrium concentrations. $K_L$ (L·mg$^{-1}$) and $K_F$ (mg g$^{-1}$) represent the Langmuir and Freundlich constants, respectively, and $n$ and $R_L$ (dimensionless) represent the Freundlich intensity and system separation factor, respectively.

Adsorption isotherms fitted by the linear regression technique are shown in Figure 5 and Table S2. The obtained Langmuir model correlation coefficient ($R^2 = 0.9995$) was higher than the Freundlich model correlation coefficient ($R^2 = 0.4810$), which means that the Langmuir model was in good accord with reality.
Therefore, MB adsorption on ZIF-67-0.2 HPW is a monolayer process with a theoretical $q_{\text{max}}$ of 446.4 mg g$^{-1}$. Moreover, the $R_{\text{c}}$ value ranged from 3.97 to $30.89 \times 10^{-3}$ which were all in 0–1, confirming that the adsorption was favorable.\(^{(9)}\)

MB removal data were fitted by thermodynamic models shown as eqs 9–10\(^{(10)}\) to evaluate the spontaneity of adsorption.

\[
\Delta G = -RT \ln K_C \\
\ln K_C = \frac{-\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R}
\]

where the universal gas constant $R$ is 8.314 J mol$^{-1}$ K$^{-1}$, $T$ (K) represents the solution temperature, $K_C$ (dimensionless) is obtained from the Langmuir model, $\Delta G$ and $\Delta H$ (kJ mol$^{-1}$) are changes of Gibbs free energy and enthalpy, respectively, and $\Delta S$ (J mol$^{-1}$ K$^{-1}$) is the change of entropy.

As seen in Figure S2 and Table 2, the negative $\Delta G$ suggested the spontaneity of adsorption. Furthermore, the decrease of $\Delta G$

Table 2. Calculated Thermodynamics Parameters

| $T$ (K) | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) |
|--------|----------------|----------------|----------------|---|
| 288.15 | -22.22 | 72.16 | 327.98 |
| 298.15 | -25.92 | | |
| 308.15 | -28.76 | | |

values confirmed that the spontaneity raise of MB adsorption resulted from temperature change, and the $\Delta H > 0$ value demonstrated that the adsorption is a decalvence process.\(^{(12)}\)

**Effect of pH and Recycling.** The adsorbent surface properties and the degree of solute ionization can be altered by pH values.\(^{(33)}\) The adsorption amount of ZIF-67-0.2 HPW kept stable within the pH range from 3 to 11 (Figure 6a), indicating that ZIF-67-0.2 HPW has good adaptability to the change of pH values. Figure S3 shows that ZIF-67 surface turned into electronegative or became more negative after the introduction of HPW, which could enhance the electrostatic attraction of the adsorption sites for cationic MB dye and greatly improved its adsorption capacity in pH values of 3.0–11.0. The regeneration and reuse of adsorbents is important for practical application. As shown in Figure 6b, the removal rate decreased to 87.2% after eight cycles.

**Effect of Ions and Dye Type.** In order to study the effect of coexisting ions on the adsorption process, NaCl, ZnCl$_2$, and CaCl$_2$ were selected as interference sources. Figure 7a shows that as the salt ion concentration increased from 0 to 0.2 mol L$^{-1}$, the removal rate of MB reduced to about 89%. The result exhibited that the existence of salt ions has a negative effect on electrostatic adsorption, leading to a little decrease in the adsorption of cationic dyes. The reason for the decrease of adsorption capacity is ascribed to the cations in the solution that are adsorbed to the adsorption sites on the negatively charged adsorbent surface.\(^{(44)}\) This confirmed that the adsorption of MB onto ZIF-67-n HPW was mainly through electrostatic attractions.

In order to study the effect of dyes on adsorption, 20 mg of ZIF-67-0.2 HPW was added to 80 mL solution of anionic dye MO. The adsorption capacity of cationic dye MB by negatively charged ZIF-67-0.2 HPW was greater than that of anionic dye MO as shown in Figure 7b. The difference in the adsorption of the two types of dyes could be attributed to the electrostatic adsorption of cationic dyes and the repulsion of anionic dyes during adsorption.\(^{(33)}\) This result also shows that electrostatic adsorption is the main driving force for the adsorption of MB by ZIF-67-0.2 HPW. The adsorption capacity of MB by ZIF-67-0.2 HPW was compared with other adsorbents reported and ZIF-67-0.2 HPW has a better adsorption performance than that of bare ZIFs and other MOF-based adsorbents (Table S1, Supporting Information).

**Adsorption Mechanism.** FTIR spectra (Figure 8a) of MB and fresh and used ZIF-67-0.2 HPW were compared.\(^{(33)}\) The used ZIF-67-0.2 HPW revealed characteristic peaks of MB (1598, 1488, 1393, 1247 cm$^{-1}$) and ZIF-67-0.2 HPW, which can indicate the successful adsorption of MB on ZIF-67-0.2 HPW. By comparing the zeta potential of ZIF-67 before and after HPW modification and the relationship between the difference of adsorption capacity and zeta potentials, it can be concluded that the potential difference has a great impact on the adsorption. At the same time, when there was competitive adsorption of cations in the solution system, the adsorption capacity of MB would be reduced. Based on above analysis, it is inferred that electrostatic interaction is the main driving force of MB adsorption. Moreover, it was also studied that ZIF-67-0.2 HPW had only a low adsorption capacity for anionic dye MO, which was also consistent with the proposed adsorption mechanism. In}

![Figure 6](https://doi.org/10.1021/acsomega.2c00377)  
**Figure 6.** pH value impact on equilibrium adsorption amount (a) (25 °C, equilibrium time = 2 h) and ZIF-67-0.2 HPW adsorption reusability for MB (b) (25 °C, pH = 6.5, equilibrium time = 2 h).
addition, the aromatic ring in MB showed a stretching vibration peak at 1598 cm\(^{-1}\), indicating the possible \(\pi-\pi\) interaction during adsorption. Possible adsorption mechanisms of MB onto ZIF-67-0.2 HPW are presented in Figure 8b.

**CONCLUSIONS**

Herein, ZIF-67-\(n\) HPW (\(n = 0.05, 0.2, 0.4\)) composites were fabricated in a facile way and applied for MB adsorption. The HPW-deposited ZIF-67 showed a high adsorption capability of 446.4 mg g\(^{-1}\) for MB. The adsorption process obeyed PSO kinetic and the Langmuir model. The driving forces of MB adsorption over ZIF-67-0.2 HPW are mainly electrostatic and \(\pi-\pi\) interactions. In addition, ZIF-67-0.2 HPW still had a high removal efficiency of pollutants after eight cycles. These studies indicated that ZIF-67-0.2 HPW is an effective and recyclable adsorbent for MB adsorption.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00377.

\(N_2\) adsorption isotherms; adsorption thermodynamics; effect of pH values on zeta potentials; and kinetic and isotherm parameters (PDF)

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Figure 7. Effect of coexisting ions on adsorption (a) (25 °C, pH = 6.5, equilibrium time = 2 h) and adsorption capacities of MB and MO by ZIF67-0.2 HPW (b) (25 °C, pH = 6.5).

Figure 8. FTIR spectra of MB and fresh and used ZIF-67-0.2 HPW (a) and possible adsorption mechanisms of MB onto ZIF-67-0.2 HPW (b).
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00377

Notes
The authors declare no competing financial interest.

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