Preparation and Characterization of Cationic Water-Soluble Pillar[5]arene-Modified Zeolite for Adsorption of Methyl Orange

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ABSTRACT: A novel quaternary cationic pillar[5]arene-modified zeolite (WPAS/zeolite) was prepared via charge interaction between the cationic WPAS and natural zeolite and characterized by scanning electron microscopy (SEM), Fourier transform infrared absorption spectroscopy, X-ray diffraction, solid-state nuclear magnetic resonance, and thermogravimetric (TG) analysis. The effects of zeolite particle size, WPAS concentration, adsorption time, initial concentration, and pH on the removal of methyl orange (MO) were studied. The SEM and XRD results revealed a strong interaction between WPAS and natural zeolite, and the modified composites showed novel microscopic morphology and structural properties. TG analysis indicated excellent thermal stability of the composite. MO was removed via electrostatic adsorption, and the removal efficiency was 84% at an initial concentration of 100 mg/L. Increase in the initial dye concentration enhanced the adsorption capacity of WPAS/zeolite and decreased the removal of MO. Based on the adsorption kinetics, the pseudo-second-order model ($R^2 = 0.998$) described the kinetic behavior of MO on WPAS/zeolite. In addition, UV and fluorescence spectra revealed that MO and WPAS are complexed by a 1:1 complex ratio, and the binding constant between them was 12595 L·mol$^{-1}$. NMR and molecular docking also verified their interaction. Therefore, the potential application of the prepared composite includes removal of organic anionic dyes.

1. INTRODUCTION

The rapid growth of cosmetic, rubber, plastic, textile, and paper industries has increased the severity of water and environmental pollution.¹ Wastewater contaminated with organic dye is recognized as one of the major sources of industrial pollution worldwide.² Each year, 700 000 tons of dyes are consumed by the textile industry. Therefore, untreated effluents discharged by the printing and dyeing industry are one of the important causes of water pollution.³ The composition of printing and dyeing wastewater is complex and extremely toxic to the ecosystem, and it is highly difficult to remove the organic dye molecules.⁴,⁵ Methyl orange (MO) ($C_{14}H_{14}N_{3}NaO_{3}S$; MO; Figure 1), an anionicazo dye, is carcinogenic and mutagenic, in addition to triggering shock, increasing heart rate, inducing jaundice, vomiting, and tissue necrosis.⁶⁻¹⁰ Treatment methods for dye removal from water include oxidation, membrane separation, coagulation, adsorption, chemical reduction, and biological treatment.¹¹⁻¹³ Adsorption is economical and effective because of its simplicity and high efficiency.¹⁴

Natural zeolite has been widely used in the aqueous treatment of environmental contaminants because of its wide variety, abundant reserves, low price, and simplicity of processing technology.¹⁵,¹⁶ Zeolite has a unique structure comprising an aluminosilicate skeleton and abundant intra-crystalline pores, resulting in strong ion exchange and adsorption properties.¹⁷,¹⁸ However, zeolites exhibit a permanent negative electrical structure due to isomorphous replacement, which results in weak adsorption of organic anions. Therefore, modification of natural zeolites has been attempted to address the issue.¹⁹,²⁰

Macrocyclic compounds playing an increasingly important role in the treatment of Pillararene was initially discovered by Ogoshi in 2008.²¹ It has a tubular morphology compared with other macrocyclic molecules such as crown ether,²² cyclodextrin,²³⁻²⁵ calixarene,²⁶,²⁷ and cucurbituril.²⁸ Pillararenes have been widely used in gas adsorption,²⁹,³⁰ wastewater treatment,³¹⁻³³ drug transport,³⁶⁻³⁹ and molecular recognition,⁴⁰⁻⁴³ due to their easy modification, simplicity of preparation, and optimal performance.³⁴,³⁵

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In this work, we report the preparation and characterization of water-soluble pillar[5]arene-modified zeolite (WPA5/zeolite). Subsequently, the adsorption of modified zeolite on MO was studied (Figure 1). In addition, the effects of zeolite particle size, initial dye concentration, adsorption time, and pH on the adsorption process were investigated. To the best of our knowledge, studies investigating WPA5/zeolite for MO dye removal have yet to be reported. Therefore, the primary aim of this work is the development of a novel method of zeolite modification, with potential application in the field of water pollution treatment.

2. RESULTS AND DISCUSSION

2.1. SEM and Optical Microscopic Analysis. The morphologies of WPAS, zeolite, and their composites were investigated via scanning electron microscopy (SEM) (Figure 2). The microstructure of WPAS was characterized by a planar structure with irregular lines. The natural zeolite exhibited an uneven sheet-like structure, with clearly visible crevice lines between the sheets. However, the WPAS/zeolite appeared as a large, irregular, and spherical structure, and the original sulcus of natural zeolite was filled. The WPAS/zeolite varied in size and shape with WPAS and natural zeolite, which confirmed the formation of novel composite materials.

The morphologies of WPAS/zeolite and natural zeolite after adsorption of MO were determined using optical photomicroscopy (Figure 3). As shown in the figure, the WPAS/zeolite was dyed deep orange after MO adsorption. However, the permanent negative charge of natural zeolite resulted in an electrostatic repulsion between the MO and the zeolite.
Therefore, the natural zeolite displayed a light orange color upon MO adsorption.

2.2. FTIR Analysis. Figure 4 shows the Fourier transform infrared absorption spectroscopy (FTIR) spectra of WPA5, zeolite, and their composite. The peak at 474.00 cm$^{-1}$ represents the bending vibration of the Si–O bond, and the peak at 539.42 cm$^{-1}$ denotes the telescopic vibration of the Si–O–Al. The peak at 1098.84 cm$^{-1}$ represents the stretching vibration of Si–O– in the zeolite structure. The characteristic peak of –OH is observed at 3433.87 cm$^{-1}$, and the peak at 3619.86 cm$^{-1}$ indicates stretching vibration generated by –OH combined with Si. In addition, the peak at 1209.84 cm$^{-1}$ in the spectrum of WPA5 suggests a telescopic vibration of the C–N bond. The peak at 1404 cm$^{-1}$ corresponds to the bending vibration of CH$_3$–N$, and the peak at 1484.36 cm$^{-1}$ denotes shear vibration of the –CH$_2$–N$^+$ bond. The vibrations of CH$_3$–N$^+$ and –CH$_2$–N$^+$ in WPA5 are found in the FTIR spectrum of the modified zeolite but not in the natural zeolite. Therefore, this phenomenon suggests successful synthesis of WPA5-modified zeolite.

2.3. XRD Analysis. Figure 5 displays the X-ray diffraction (XRD) patterns of WPA5, zeolite, and the WPA5/zeolite composite. The XRD pattern of WPA5 reveals its amorphous structure. The natural zeolite yields major crystal diffraction peaks at 12.36°, 20.85°, 21.97°, 23.59°, 24.86°, 26.62°, 27.65°, 36.07°, 36.52°, 39.45°, 50.15°, and 59.93°. However, the significant characteristic peaks of natural zeolite at 27.65° and 36.52° were not observed in the WPA5/zeolite composite, and the major peaks of zeolite were weakened in the composites, which indicated the strong interaction between WPA5 and zeolite.

2.4. SSNMR Analysis. The formation of WPA5/zeolite was further confirmed using $^{13}$C SSNMR analysis (Figure 6). The peaks located between 10 and 70 ppm (α) were assigned as methyl (–CH$_3$) and methylene (–CH$_2$–) in WPA5 (Figure 6a), and the peaks located between 110 and 210 ppm (β, γ) can be resolved into the sp$^2$ carbons of the phenyl rings in the WPA5. The carbon peaks in WPA5 can be clearly found in the $^{13}$C SSNMR spectrum of WPA5/zeolite (Figure 6b), and no carbon signal is detected in natural zeolite (Figure 6c). These phenomena strongly illustrate the successful preparation of WPA5-modified zeolite.

2.5. TG Analysis. The thermogravimetric (TG) curves of WPA5, zeolite, and WPA5/zeolite are shown in Figure 7. The melting point of WPA5 ranges from 271.2 to 271.8 °C, suggesting small amounts of bound and free water in WPA5. A weight loss of 11.84 wt % occurred initially when the temperature increased to 290 °C. A major weight loss of WPA5 (64.88 wt %) in the region of 300–390 °C suggested degradation. The final weight loss at 390–780 °C (28.49 wt %) revealed the decomposition of WPA5. However, the entire
warming process had little effect on the weight loss (4.05%) of natural zeolite. Notably, the total weight loss of the WPAS/zeolite was 8.89 wt%, indicating the loading of a specific WPAS mass onto the zeolite. In addition, TG analysis demonstrated that zeolite increased the thermal stability of WPAS.

2.6. Adsorption Study. 2.6.1. Standard Curve of MO. The standard curve of MO is shown in Figure 8. It was calculated using the equation 

\[ C = \frac{(A + 0.02331)}{0.07891} \]

and it has a correlation coefficient of \( R = 0.9999 \).

![Figure 8](image)

Figure 8. Standard curve of MO.

2.6.2. Effect of Zeolite Particle Size. The percent removal of MO by zeolites and WPAS/zeolite of different particle sizes is shown in Figure 9. The removal of MO by natural zeolite was very limited, and the average removal efficiency was about 4%. The adsorption of MO by natural zeolite was greatly improved after modification with WPAS. Doping of WPAS onto the surface and pores of the zeolite via charge interaction resulted in a positive charge and facilitated the removal of the anionic pollutant MO. When the particle size was reduced from 10 to 30 mesh, the adsorption of MO by the WPAS/zeolite was continuously increased to a maximum of 85% at 30 mesh. When the particle size was decreased, the removal of MO by the WPAS/zeolite also declined. The reduced particle size increased the specific surface area of the zeolite, which provided additional ion exchange sites for the binding of WPAS molecules to the zeolite. When the particle size was reduced, the increased specific surface area of the zeolite provided additional ion exchange sites, facilitating the binding of WPAS molecules to the zeolite. However, the decreased space was not conducive to WPAS binding to the surface of the zeolite and thus the percent removal of MO was reduced.

2.6.3. Effect of WPAS Concentration. The effect of different concentrations of WPAS-modified natural zeolite (30 mesh) on the removal of MO is shown in Figure 10. The removal efficiency of MO by natural zeolite was 4.4% and that of MO by WPAS/zeolite dissolved in 0.5 g/L WPAS solution was 16.2%. With the increased WPAS concentration, the percent removal of MO by WPAS/zeolite was also increased. When the WPAS concentration was 3.5 g/L, the removal of MO by the WPAS/zeolite reached 81.4%. As the WPAS concentration continued to increase, the removal of MO by the modified zeolite tended to increase slowly, but this increase was not significant. When the WPAS concentration was 8.0 g/L, the removal of MO by the WPAS/zeolite reached 84.6%. Based on the dosage of WPAS and the percent removal of MO, the WPAS solution at a concentration of 8.0 g/L was selected to modify the zeolite in a subsequent study.

2.6.4. Effect of Contact Time. The effect of adsorption time on MO removal is shown in Figure 11. In general, as the adsorption time was prolonged, the percent removal increased. The rapid adsorption from 0 to 150 min was partly attributed to insufficient internal diffusion resistance and a substantial number of adsorption sites. When the adsorption time increased to 150 min, the removal of MO by the modified zeolite was 75.45%. After 150 min, the concentration of MO gradually decreased, which led to a decrease in the concentration gradient between the solution and the zeolite surface. Hence, the diffusion resistance was increased, and the adsorption rate declined. The percent removal of MO by the modified zeolite increased very slowly and reached 81.51% in 960 min.

2.6.5. Effect of Initial Concentration. The initial concentration of MO plays an important role in the removal of the contaminant by allowing the dye molecule to overcome the mass transfer resistance generated from the aqueous to the solid phase. As shown in Figure 12, different initial concentrations of MO solution affect the dye removal and adsorption capacity. It is apparent from the figure that the percent removal of MO by the modified zeolite decreases as the initial concentration increases due to the decreased number of active sites in the modified zeolite.

2.6.6. Effect of pH. Solution pH is a meaningful parameter in the adsorption of pollutants. It changes the efficiency of MO adsorption by regulating the surface charge and dissociation of the zeolite. The effect of pH on the removal of MO is shown in
It is apparent that the WPA5/zeolite showed an "M" shape for the percent removal of MO in the pH range of 2–12 and reached a maximum at pH 5. Subsequently, the percent removal declined to a minimum at pH 7. However, as the pH increased from 7 to 9, the removal was enhanced and reached a maximum at pH 9. However, as the pH continued to increase, the surface of the WPAS/zeolite attracted OH\(^{-}\) ions more efficiently than MO with a large molecular structure. This factor mainly contributed to the reduction of MO clearance by WPAS/zeolite at a high pH.

2.7. Adsorption Kinetics. Two kinetic models (pseudo-first-order and pseudo-second-order models) were used to study the adsorption mechanism of modified zeolites. Pseudo-first-order models have been widely used to study the adsorption behavior of solid/liquid systems. The linear form of the model is represented by the following equation

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]

In the above equation, the term \( q_t \) (mg·g\(^{-1}\)) denotes adsorption capacity at time \( t \), \( q_e \) (mg·g\(^{-1}\)) represents adsorption capacity at equilibrium, and \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order-rate constant.

The linear form of the pseudo-second-order model is represented by the following formula

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

The second-order-rate constant \( k_2 \) and the equilibrium adsorption capacity \( q_e \) can be determined from the \( t/q_t \) versus \( t \) curve.

The linear plots of pseudo-first-order and pseudo-second-order models for MO adsorption by WPAS/zeolite are shown in Figure 14. The correlation coefficients are listed in Table 1. The goodness of fit can be determined by fitting the linear regression coefficient \( R \) of the straight line. In addition, the degree of closeness between the adsorption capacity obtained via comparison of \( q_{e,exp} \) and \( q_{e,cal} \) obtained experimentally can also be used as a basis for the determination of the goodness of fit of the kinetic model. The correlation coefficient \( R \) (0.966) of the pseudo-first-order model was lower than that of the pseudo-second-order model, and there was a large deviation between its theoretical adsorption capacity \( q_{e,cal} \) (2.08) and the experimental adsorption capacity \( q_{e,exp} \) (4.04). The \( R^2 \) value of the pseudo-second-order model was 0.996, and the pseudo-second-order theoretical adsorption capacity \( q_{e,cal} \) (3.88) was close to the experimental value. Therefore, the pseudo-secondary-model is more efficient in describing the adsorption behavior of MO on WPAS/zeolite.

2.8. Adsorption Isotherm. Adsorption thermodynamics studies are important in delineating the adsorbent–adsorbate interactions and the design of adsorption systems. Langmuir and Freundlich isotherms have been widely used because of fewer parameters and simplicity, with a high degree of fitness to the adsorption behavior of solid–liquid systems.

The Langmuir equation is expressed as follows

\[ q_e = \frac{q_m K_L C_v}{1 + K_L C_v} \]

The equation for the linear change of eq 3 is as follows

\[ \frac{C_v}{q_e} = \frac{C_v}{q_m} + \frac{1}{K_L q_m} \]
where $q_e$ is the equilibrium adsorption capacity of the adsorbent (mg g\(^{-1}\)), $C_e$ denotes the equilibrium concentration of the adsorbate (mg L\(^{-1}\)), $K_L$ represents the Langmuir constant (L/mg), and $q_m$ refers to the maximum adsorption capacity (mg g\(^{-1}\)).

The separation factor or equilibrium parameter is expressed by the following formula

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} \text{(5)}$$

In the above equation, if $R_L > 1$, the isotherm nature is unfavorable; linear if $R_L = 1$; favorable if $0 < R_L < 1$; and irreversible if $R_L = 0$.

The Freundlich isotherm model is an empirical formula used for the determination of multimolecular layer adsorption, which has a certain degree of generality. The most common type of adsorption isotherm equation is as follows

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} \text{(6)}$$

The linearized form of the Freundlich isotherm model is as follows

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

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### Table 1. Adsorption Kinetic Parameters of MO on WPAS/Zeolite

| exp $q_{e,exp}$ (mg g\(^{-1}\)) | $K_1$ (min\(^{-1}\)) | $q_e$ (mg g\(^{-1}\)) | $R^2$ | $K_2$ (g mg\(^{-1}\) min\(^{-1}\)) | $q_e$ (mg g\(^{-1}\)) | $R^2$ |
|---------------------------------|----------------------|------------------------|------|----------------------|------------------------|------|
| 4.04                            | 0.0143               | 2.08                   | 0.966| 2.96                 | 3.88                   | 0.999|
concentrations, by a nonlinear least squares method according to the curve-fitting eq 10.

\[
K_s = \frac{[\text{MO}/\text{WPAS}]}{([\text{MO}]_0 + [\text{WPAS}]_0 + 1/K_s)} \\Delta A \epsilon \]

\[
\Delta A = \Delta \epsilon ([\text{MO}]_0 + [\text{WPAS}]_0 + 1/K_s) \\
\pm \sqrt{\Delta \epsilon^2 ([\text{MO}]_0 + [\text{WPAS}]_0 + 1/K_s)^2 - 4\Delta \epsilon^2 [\text{MO}]_0 + [\text{WPAS}]_0} \\
/2
\]

where \([\text{MO}/\text{WPAS}],[\text{MO}], [\text{WPAS}], [\text{MO}]_0\) and \([\text{WPAS}]_0\) are the equilibrium concentrations of the \text{MO}/\text{WPAS}, \text{MO}, \text{WPAS}, and the original concentrations of \text{MO} and \text{WPAS}, respectively (mM); \(\Delta A\) indicates the change in absorbance of \text{WPAS} in the presence or absence of \(\text{MO}\); and \(\Delta \epsilon\) is the differential molar extinction coefficient of \text{WPAS} in the absence and presence of \(\text{MO}\).

We obtained the complex stability constant for the \text{MO}/\text{WPAS} via a nonlinear least squares curve-fitting method. The stability constant \(K_s\) and Gibbs free energy \(\Delta G\) of the inclusion complex of \text{WPAS} and \text{MO} in the aqueous phase are 12595 L·mol⁻¹ (log \(K_s\) = 4.0995) and −23.403 kJ·mol⁻¹, respectively. It can be seen from the inset in Figure 16a that there is a good linear match between the experimental value and the theoretical value, which shows the 1:1 stoichiometry of the \(\text{MO}/\text{WPAS}\) inclusion complex.

As shown in Figure 16b, \text{WPAS} has a fluorescence peak at 235 nm. With the addition of different concentrations of \text{MO}, the fluorescence of \text{WPAS} gradually decreases. This indicates that the fluorescence properties of \text{WPAS} are significantly changed after complexing with \text{MO}. Furthermore, Job’s method was employed to obtain the stoichiometry of \text{MO} and \text{WPAS} via the fluorescence spectroscopy. In Figure 16c, the value of the max mole fraction of \text{MO} in this work is 0.5, which strongly proves the formation of the \text{MO}/\text{WPAS} inclusion complex with a stoichiometry of 1:1. The molecular docking diagram of \text{WPAS} and \text{MO} is shown in Figure 17. MO ran through the cavity of \text{WPAS} and was at the geometric center of \text{WPAS}. Then, the entire \text{MO} molecule was encapsulated by \text{WPAS}, at which time \text{MO} was docked on the inner wall of \text{WPAS}, eventually forming an \text{MO}/\text{WPAS} coordination complex.

\(1^H\) NMR data confirmed the \text{MO} and \text{WPAS} complexation in water. As shown in Figure 18, after adding the equivalent amount of \text{MO} to \text{WPAS}, the signal of the proton signal of the host and the guest exhibits a significant shift or signal broadening effect. Thus, \text{MO} should be more deeply incorporated into the macrocycle cavity of \text{WPAS}. Furthermore, the 2D NMR \(1^H-1^H\) NOESY of the complexes confirms host–guest complexation (Figure 19). The aromatic

Figure 16. (a) Ultraviolet titration of the WPAS and MO in water: \(4 \times 10^{-5}\text{ mol·L}^{-1}\) WPAS, 0.05–1 equiv of MO. (b) Fluorescence spectroscopy titration of the WPAS and MO in water: \(2 \times 10^{-5}\text{ mol·L}^{-1}\) WPAS, 0.1–1.5 equiv of MO, 285 nm excitation wavelength, slit = 5/5 nm. (c) Job’s plot for determining the stoichiometry in the complex of the WPAS and MO in water. (d) Variation of the absorption of WPAS upon addition of MO in water: \(3 \times 10^{-5}\text{ mol·L}^{-1}\) MO, 0.2–3 equiv of WPAS.

Figure 17. Optimal conformation formed by docking MO to the cavity of WPAS.
protons of MO (D, C, E) have cross-peaks with H1, H3, and H4 of WPAS. The aromatic protons of MO (B) have cross-peaks with H1 and H3 of WPAS. Thus, we can conclude that the MO/ WPAS inclusion complex is formed.

The removal ability of pure WPAS to MO is shown in Figure 16d. The UV absorption of MO exhibits a blue shift and small decreases with the addition of WPAS. However, the modified zeolite does not undergo a blue shift when adsorbing MO, and the absorbance is remarkably lowered (Figure 11). In addition, WPAS is water-soluble; it does not remove the MO from the aqueous phase and does not achieve the purpose of treating sewage. This experiment reveals the correctness of the experimental scheme for the adsorption of MO by WPAS-modified zeolite.

3. CONCLUSIONS

This study focused on the development of a novel, environmentally friendly WPAS/zeolite for the adsorption of MO from aqueous solutions. The SEM, XRD, FTIR, and SSNMR characterizations indicated successful adsorption of WPAS on the surface of the zeolite. TG examinations confirmed the thermal stability of the WPAS/zeolite. The effects of zeolite particle size, WPAS concentration, adsorption time, initial concentration, and pH on the percent removal efficiency of MO were also investigated. The kinetic and adsorption data indicated that the adsorption of MO on the WPAS/zeolite could be best described using linear forms of pseudo-second-order models. In addition, UV and fluorescence spectroscopy, NMR, and molecular docking provided an in-depth analysis of the mechanism by which WPAS interacts with MO. The WPAS/zeolite is a promising candidate for the removal of MO.

4. EXPERIMENTAL SECTION

4.1. Materials. Natural zeolite was purchased from Hengnuo Filter material Co. Ltd. (Henan Province, P.R. China). MO, hydroquinone bis(2-hydroxyethyl)ether, paraformaldehyde, tetramethylethylenediamine, triphenylphosphine, boron trifluoride etherate (98%), and trimethylamine (30%) were purchased from Shanghai Titan Technology Co. Ltd. All of the reagents used were of analytical grade (A. R.). All of the aqueous solutions were prepared using ultrapure water.

4.2. Synthesis of WPAS. WPAS was synthesized as described in the Supporting Information (Figure 1).

A solution of CBr4 (33.46 g, 100.90 mmol) in acetonitrile (250 mL) was added dropwise to the acetonitrile (50 mL) of hydroquinone bis(2-hydroxyethyl)ether (10.0 g, 50.45 mmol) and PPh3 (36.46 g, 100.90 mmol) under an atmosphere of nitrogen and reacted at room temperature for 4 h to obtain compound 2 (82%). To a solution of compound 2 (3.24 g, 10.00 mmol) in 1,2-dichloroethane (100 mL), paraformaldehyde (0.90 g, 30 mmol) was added under nitrogen atmosphere; this was followed by the addition of BF3 OEt2 (1.39 mL, 10 mmol) to the solution. The mixture was stirred at room temperature for 6 h, resulting in a green solution. After the solvent was concentrated in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:1 v/v) as the eluant to yield compound 3 (40%) as white powder. Compound 3 (0.4813 g, 0.2865 mmol) and excessive trimethylamine (3.2 mL, 11.46 mmol) were added to ethanol (30 mL). The solution was refluxed for 36 h. The solvent was concentrated in vacuo, and 10 mL of deionized water was added. After filtration, a clear solution was obtained. Finally, the water was concentrated in vacuo to yield compound 4 (91%), with the following spectroscopic features: 1H NMR (400 MHz, D2O) δ (ppm): 6.89 (s, 10H), 4.49 (s, 10H), 3.84 (s, 20H), 3.24 (s, 90H); 13C NMR (100 MHz, D2O) δ (ppm): 149.30, 129.89, 116.55, 64.91, 63.49, 54.13, 29.57.

4.3. Preparation of the WPAS/Zeolite Composite. The zeolite was added to a WPAS solution (10 mL of WPAS aqueous solution per 1 g of zeolite). The mixture was shaken at room temperature for 24 h; this was followed by filtration of the solution. The WPAS/zeolite composite was repeatedly washed with ultrapure water (40 mL × 3) and finally dried at 50 °C to constant weight.

4.4. Characterization. 1H and 13C NMR spectra were recorded on a Bruker AVANCE 400 nuclear magnetic resonance spectrometer using tetramethylsilane as the internal standard. SSNMR data were recorded on JNM-ECZ600R. The absorbance was measured using an Agilent 8453 UV—vis spectrometer. The fluorescence data were recorded on a Cary Eclipse fluorescence spectrophotometer. The FTIR spectra were measured with a Thermo Nicolet Avatar 360 spectrometer using the KBr pellet. XRD patterns of powder samples were recorded using a D/Max-3B diffractometer with Cu Kα radiation (λ = 0.15406 nm, 100 mA, 40 kV). The scan rate was 5°/min, and the range of 2θ = 0.02° varied between 3° and 80°. The sample microstructure was analyzed using a...
4.5. Adsorption Experiments. 4.5.1. Standard Curve of MO. Aliquots of 100 mL containing 150 mg/L MO solution were configured accurately, and the following volumes of MO solution were added to a 10 mL volumetric flask: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mL. After ensuring a constant volume, the flasks were shaken. The absorbance was measured at the maximum absorption wavelength (467 nm).

4.5.2. Effect of Zeolite Particle Size. The zeolite was divided into different sizes, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mesh, using a standard sampling sieve. A 10 g/L WPAS solution was added to the zeolite and shaken for 24 h; this was followed by removal of the supernatant and washing with ultrapure water. Finally, the zeolite was dried at 50 °C to obtain a constant weight. Zeolite particles of different sizes and weighing 0.5 g each were transferred to a 50 mL stoppered conical flask containing the WPAS/zeolite mixture; this was followed by the addition of 25 mL of the 100 mg/L MO solution and shaking at room temperature for 12 h. After standing for 1 h, the UV absorption spectrum was measured, and the concentrations of MO before and after adsorption were determined from the standard curve of MO.

The adsorption amount (q) and removal percentage (R) of the modified zeolite for MO were calculated using the following equations

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  \hspace{1cm} (11)

\[ R = \frac{(C_0 - C_e)}{C_0} \times 100\% \]  \hspace{1cm} (12)

4.5.3. Effect of WPAS Concentration. A series of WPAS solutions with concentrations ranging from 0.5 to 20 g/L (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 12, 14, 16, 18, and 20 g/L) were prepared. The zeolite was modified with different concentrations of WPAS. It was washed repeatedly with ultrapure water and dried at 50 °C to constant weight. Zeolite modified with different concentrations of aromatic hydrocarbons was accurately weighed to 0.5 g in a 50 mL conical flask. This was followed by the addition of 25 mL of the 100 mg/L MO solution and shaking at room temperature for 12 h. The absorbance was measured after centrifugation at 3000 rpm for 10 min.

4.5.4. Effect of Contact Time. A batch of modified zeolite was prepared using 8 g/L of WPAS solution and 30 mesh zeolite. About 0.5 g of zeolite was added into a 50 mL stoppered conical flask and mixed with 25 mL of a 100 mg/L MO solution. The mixture was oscillated at room temperature for different times (10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330, 360, 420, 480, 540, 600, 660, 720, 780, 840, 900, and 960 min), and the removal percentage of MO by the modified zeolite was calculated according to the method described in Section 4.5.2.

4.5.5. Effect of Initial Concentration. After configuring a series of concentrations of MO solution (20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, and 300 mg/L), the adsorption experiments were conducted by the addition of 0.5 g of modified zeolite.

4.5.6. Effect of pH. A specific concentration of MO solution was obtained by adjusting the pH (2–12) of the aqueous solutions using HCl and NaOH.

4.6. Interaction between WPAS and MO. 4.6.1. Determination by UV and Fluorescence Spectroscopy. An in-depth study of the host–guest interaction between WPAS and MO helps us to understand the adsorption mechanism. To quantify the complexation of the MO by WPAS, the stability constants of the MO/WPAS complexes formed in water were estimated by ultraviolet titration. The concentration of WPAS was held constant at 0.04 mM. Then, an appropriate amount of MO was added, and the final concentrations varied from 0 to 0.04 mM (MO: 0, 0.002, 0.004, 0.006, 0.008, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.024, 0.026, 0.028, 0.03, 0.032, 0.034, 0.036, 0.038, and 0.04 mM in water). In addition, the fluorescence properties of the supramolecular system of MO with WPAS were investigated by fluorescence spectroscopy titration. The concentration of WPAS was held constant at 0.02 mM. Then, an appropriate amount of MO was added, and the final concentrations varied from 0 to 0.03 mM (MO: 0, 0.002, 0.004, 0.006, 0.008, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.024, 0.026, 0.028, and 0.03 mM in water). The spectral data were recorded after waiting for 30 min. The UV and fluorescence spectra were recorded in the 280–500 nm spectral range. For fluorescence tests, the excitation wavelength was 285 nm. The excitation and emission slits were set at 5/5 nm, respectively. All of the experiments were carried out in triplicate.

4.6.2. Job’s Plot Measurements. A solution of WP5A and MO at a concentration of 0.02 mM was prepared using water. First, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, and 0.0 mL of the WP5A solution were added and transferred to 5 mL volumetric flasks. Then, 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mL of the MO solution were added to each vial of WP5A solution, making the total volume of each vial 5 mL. After shaking, fluorescence spectra were recorded at room temperature.

4.6.3. Pure WPAS for the MO Removal Capability Test. We further tested the ability of pure WPAS to remove MO to verify the correctness of the MO removal scheme for WPAS-modified zeolites. The concentration of MO was held constant at 0.03 mM. Then, different equivalents of WPAS were added (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, and 3.0 equiv). The UV spectral data were recorded after vortexing for 5 min and waiting for 1 h.

4.6.4. Docking Calculation. Furthermore, in order to clearly explain the formation mechanism of the MO/WPAS complex, molecular docking calculations were performed. Docking MO to the cavity of WPAS was based on the empirical free energy function and the Lamarck genetic algorithm. WPAS acted as a rigid acceptor molecule, while the MO acted as a ligand molecule allowing for flexible twisting. The WPAS was set to a grid box size to 5.0 nm × 5.0 nm × 5.0 nm; the grid spacing was 0.375 nm. Then, we calculated the grid points. The maximum evaluation number was 2.5 × 10⁷, and the Lamarck genetic algorithm was used to perform 100 conformational searches. After the docking, the inclusion pattern of the MO/WPAS complex was discussed by cluster analysis. Molecular docking was performed on the AutoDock 4.2 program.
Synthetic of cationic water-soluble pillar[5]arene (PDF)

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