INTRODUCTION

Nowadays, water contamination problems resulting from the indiscriminate discharge of antibiotic, dye, and heavy metal pollutants have become a leading environmental issue. As a result of the highly toxic or non-biodegradable components discharged in the water, such an environmental issue not only jeopardizes human health but also can pose a significant threat to the entire ecosystem.4,5 Because dyes are highly toxic and difficult to be degraded even at low concentrations, the dye-containing wastewater has garnered significant concerns.6 In the past few decades, various methods such as physical, chemical, and biological decolorization have been used to detoxify dye wastewater and have achieved great results in the academic and industrial fields. However, many technologies are still inefficient in removing dyes, which limits their application in certain industries. Therefore, there is an urgent need to develop a simple and effective method that can effectively eliminate dye pollutants in wastewater.7

Currently, the removal of various coloring matters from wastewater by adsorption has been commonly recognized as a simple, highly efficient, easily operated, and low-cost method.8,9 A variety of adsorbents can be easily designed at the molecular level to suit the structure or type of pollutants to be treated, so these uniquely designed adsorbents can meet different application requirements.10−13 Among these adsorbents, clay minerals have been widely used to effectively remove pollutants due to their advantages of natural abundance, good stability, economical factor, and environmental friendliness.14,15 As the dominating member of the clay mineral family, attapulgite (APT), with a one-dimensional (1D) nanorod-like crystal morphology, unique nanoporous structure, and a larger specific surface area,16−18 has attracted increasing attention in recent years. APT possesses a 2:1 type ribbon-layer structure, which consists of alternatively arranged continuous SiO11 tetrahedron sheets and discontinuous octahedral sheets. Each ribbon forms a zeolite-like nanosized channel (0.37 nm × 0.64 nm) along the c-axis of the rod.18 Owing to the isomorphous substitution of trivalent cations for the divalent cations in the octahedral sheet,19−21 the surface of the APT rod is negatively charged. Even so, natural APT typically possesses fewer pores, fewer active surface groups, and low surface charges, which can lead to its poor adsorption

ABSTRACT: Attapulgite (denoted as APT, also called palygorskite) has been regarded as the green material in the “21st century world” and has attracted widespread attention due to its advantages of low cost, natural abundance, nontoxic nature, and environmental friendliness. However, the limited adsorption sites and surface charges of natural APT greatly hinder its application as an adsorbent in industrial fields. In this work, natural APT was modified with sodium humate (SA) via a facile one-step hydrothermal process to improve its adsorption capacity and systematically studied its ability to remove methylene blue (MB) from aqueous solutions. The effect of hydrothermal modification in the presence of SA on the microscopic structure, morphology, and physicochemical properties of APT was studied by field-emission scanning electron microscopy, Fourier transform infrared spectrometry, X-ray diffraction, and Brunauer–Emmett–Teller analyses. The adsorption properties of the modified APT toward MB were evaluated systematically. The results demonstrated that the modified APT has a high adsorption capacity of 227.27 mg/g and also shows a high removal rate up to 99.7% toward MB in a dye solution with an initial concentration of 150 mg/L, which was a 64.7% increase as compared to that of raw APT. The adsorption kinetics could be fitted to the pseudo-second-order model, while the adsorption isotherm could be well-described with the Langmuir model. It was concluded that electrostatic attraction, hydrogen-bonding interaction, and chemical association are the main driving force during the adsorption process.
capability. Therefore, it is highly desired to modify APT using a facile yet effective method in order to enhance its adsorption properties and extend its application in more fields.

Thus far, many conventional methods, that is, acid treatment, heat treatment, and organification of surface, have been employed to modify natural APT so as to increase its adsorption capacity. However, these conventional methods, which are based on dispersing the crystal bundles and partially breaking the Si—O—M bond, can only enhance the adsorption properties of APT to a limited extent. As such, drastic improvements in the adsorption properties of APT are scarcely realized by using these common methods. In contrast, the hydrothermal process has frequently been regarded as a feasible method to modify clay, and it has been shown to enhance the adsorption performance of the clay minerals.

To date, modifying APT with the hydrothermal process has been studied, and the adsorption capacity of APT toward dyes and heavy metal ions could be enhanced by treating it with hydrothermal modifications in our previous studies. These previous works have confirmed that utilizing both the hydrothermal process and surface functionalization is an extremely effective approach to enhancing the adsorption capacity of APT. Our preliminary research work also found that the modification of APT with organic molecules containing certain functional groups is effective to enhance its adsorption performance toward dyes. In contrast to other synthetic chemicals, sodium humate (SA) is a nontoxic, low-cost, and contaminant-free natural organic molecules with rich carboxyl or hydroxyl functional groups, which has potential to be used to modify APT and thus improve its adsorption performance. Therefore, in this work, natural APT was modified with SA via a hydrothermal process to produce a high-efficiency adsorbent for the removal of dyes. The SA-functionalized APT was characterized by Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and zeta potential techniques to investigate the effects of hydrothermal functionalization on the structure and adsorption properties of APT. In addition, the adsorption properties of modified APT were evaluated by systematic adsorption experiments for methylene blue (MB) dye.

**MATERIALS AND METHODS**

**Materials.** Raw APT was provided by Dingbang Mineral Products Sci-Technology Co. Ltd. (Jiangsu, China). SA (C₉H₈Na₂O₄; MW 226.14; AR grade) was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). MB (indicator grade), with the molecular formula of C₁₆H₁₈N₃SCl, was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China), and it was used without any further purification. All other reagents were of analytical grade, and all solutions were prepared using deionized water.

**Preparation of the Hydrothermally Modified APT.** Raw APT was uniformly dispersed in 60 mL of the aqueous solution consisting of SA and deionized water with a solid/liquid ratio of 1/200 (m/v) under continuous mechanical stirring. Then, the resultant dispersion was transferred to a 100 mL sealed stainless steel reactor with Teflon inner, and it was reacted at 180 °C for 2 h. The reactor was then allowed to cool naturally to room temperature, and the suspension was later centrifuged at 4000 rpm (the centrifugal force is 3000g) for 10 min to separate the solid product from the liquid. The solid product was washed with deionized water until the pH of the supernatant was nearly neutral. Subsequently, the washed product was vacuum-dried at 60 °C for 12 h until it reached a constant weight. Finally, the dried product was crushed, ground, and sieved through a 200-mesh screen. The raw APT and the modified APT prepared via the hydrothermal process were labeled as UAPT and SA(x)-APT (where x represents the SA concentration), respectively. The preparation process of the adsorbent is illustrated in Scheme 1.

**Scheme 1. Schematic Illustration of the Synthetic Route of the SA-APT Materials**

**Batch Adsorption Experiment.** A typical adsorption experimental procedure is as follows: 0.0250 g of the adsorbent was added to 25 mL of MB solution (initial concentration, 200 mg/L). The resultant mixture was shaken using a THZ-98A orbital shaker at a fixed speed of 150 rpm and a temperature of 30 °C for 2 h to achieve adsorption equilibrium. Afterward, the solid adsorbent was separated from the MB solution via centrifugation, and the supernatant was collected after the adsorption experiment. The residual MB concentration in the supernatant was determined by a Specord 760UV/Vis spectrophotometer at a maximum absorbance wavelength of 664 nm. Then, the amount of MB adsorbed per unit mass of adsorbent could be calculated according to the difference in the MB concentrations in the solutions before and after adsorption (eq 1)

\[
q_e = \frac{(C_0 - C) \times V}{W}
\]

where \(W\) (g) is the mass of the adsorbent used; \(V\) (L) is the volume of MB solution used; \(C_0\) and \(C\) (mg/L) are the concentration of MB solution before and after adsorption, respectively; and \(q_e\) (mg/g) is the amount of MB adsorbed.

**Characterization Techniques.** Zeta potential of the samples was measured using a ZS90 zeta voltmeter (Malvern, Britain). The morphology of the samples was observed under a field-emission scanning electron microscope (S4800 SEM, Hitachi, Japan). FTIR spectra of the samples were recorded using a Fourier transform infrared spectrometer (650, Tianjin Port East Technology Development Co. Ltd.) in the range of 4000–400 cm⁻¹ using KBr pellets. Powder XRD patterns of the samples were collected using an X-ray diffractometer with a Cu anode (Rigaku Ultimate IV), running at 40 kV and 200 mA. The specific surface area (S_{BET}) of the sample was determined based on the Brunauer–Emmett–Teller (BET) method. The pore volume (PV) and pore size (PSD) distribution (PSD) in the sample were estimated based on the Barrett–Joyner–Halenda (BJH) method, conducted at 77 K (ASAP 2460 V2.02, Micromeritics Instrument Corporation). TG curves were measured using a NETZSCH STA 449F5 under air flow at a heating rate of 10 °C/min to study the thermal decomposition behavior of the samples over the temperature range from 25 to 800 °C.
RESULTS AND DISCUSSION

XRD Analysis. The XRD patterns of UAPT and modified APT are presented in Figure 1. It can be clearly observed that the intensity of the main diffraction peak of APT at 2θ = 8.32° (corresponding to the (110) plane) decreases gradually with the increasing concentration of SA from 0.01 to 0.2 mol/L. However, even at the highest SA concentration, this main diffraction peak can still be detected. This result indicates that the prevailing APT crystal structure remains intact after the hydrothermal modification. The diffraction peaks located at 2θ = 13.64° (200 plane), 16.38° (130 plane), and 19.80° (400 plane) slightly weakened after the hydrothermal modification, with a more evident decrease in the peak intensity for SA(0.2)-APT. The decrease in the intensity of the diffraction peak is due to the interaction between SA and APT during the reaction. The result obtained from XRD analysis is consistent with that from field emission SEM (FESEM) images (as shown in Figure 2, whereby the modified APT rod becomes shorter).

In addition, a new diffraction peak can be observed at about 2θ = 12.40° after modification, which can be attributed to kaolinite (JCPDS no. 14-0164) indicating that a tiny part of APT was transformed as kaolin with a 2D sheet structure, which may generate synergy effects with 1D APT on improving the adsorption performance of the adsorbent. After modification, the diffraction peak corresponding to dolomite (located at 2θ = 30.98°) disappears, indicating that the dolomite impurity mineral was removed during the hydrothermal reaction. Furthermore, the diffraction peaks belonging to quartz (located at 2θ = 20.88 and 26.66°) show no obvious change after the hydrothermal modification, suggesting the stability of quartz under acidic hydrothermal reaction conditions.

FESEM Images. Figure 2 exhibits the FESEM micrographs of APT before and after the hydrothermal modification with SA. As shown in Figure 2a, the rod-like crystal bundles and agglomerates can be clearly observed in the FESEM image of UAPT, together with a large number of other associated minerals. After the hydrothermal modification of APT with different amounts of SA, there are varying changes in the morphology of the sample. As shown in Figure 2b–d, (i) the dispersion of APT rods was improved after the hydrothermal modification, and there is an increase in the number of rod-like crystals, indicating that the hydrothermal process facilitates the disaggregation of crystal bundles and agglomerates of APT; (ii) the shape of the rods shows no obvious change with the increase of SA concentration. However, after treating APT with SA-(0.05) (Figure 2c) and SA-(0.2) (Figure 2d), there is a reduction in the length of the rod-like crystal. Such an observation may be due to the interaction between SA and APT during the hydrothermal process. This can be verified by Figures S1 and S2 (see the Supporting Information), whereby there is a significant increase in the C and O contents in APT after modification (see the Supporting Information). This can be further confirmed by Table S1 (organic elemental analysis). From Table S1, the contents of C significantly increase from 0.50% (UAPT) to 18.02% [SA(0.2)-APT], and the contents of O increase from 13.38% (UAPT) to 15.53% [SA(0.2)-APT]. The above information suggests that SA molecules could interact with APT.

FTIR Analysis. FTIR was conducted to investigate the changes in the surface groups on APT. As shown in Figure 3, four shoulder bands located at about 3615 cm\(^{-1}\) can be assigned to the stretching vibration of (Mg/Al/Fe)O−H in the octahedral sheet of APT, and a slight increase in the peak intensity was observed after modification.\(^{31,32}\) Meanwhile, the band located at about 3548 cm\(^{-1}\) can be assigned to the stretching vibration of the (Si)O−H group,\(^{33}\) which weakened after being treated with the SA solution (from 0.01 to 0.2 mol/
L). As the concentration of the SA solution increases to 0.2 mol/L, the band located at about 3548 cm⁻¹ almost disappears. The new bands located at about 3690 cm⁻¹ can be attributed to the O–H stretching of the inner-surface hydroxyl groups in Al–O–H. After the modification process, a new weak band appears at 1699 cm⁻¹ (corresponding to the C=O stretching vibration of –COOH in an aromatic compound) and 1561 cm⁻¹ (assigned to the asymmetric –COO⁻ stretching vibration), which provides evidence for the interaction between SA and APT and its subsequent bonding onto its surface (SA-0.2-APT). Concurrently, several changes are observed in the FTIR spectrum for APT: (i) the band located at about 1196 cm⁻¹ (corresponding to the Si–O–Si (that connects two reverse tetrahedron sheets), and this band is a unique absorbance peak for the ribbon-layer silicate; (ii) the bands located at 979 cm⁻¹ (corresponding to the Si–O–Mg stretching vibration) almost disappear; and (iii) the band located at 1652 cm⁻¹ (corresponding to the H–O–H bending vibration modes of the adsorbed, zeolitic, and crystal water molecules) is significantly reduced in the FTIR spectrum for SA(0.2)-APT, and it almost overlaps with the peak located at 1699 cm⁻¹. These changes occurred after the modification of APT. Such results indicate that some Si–O–Si and Si–O–M bands are broken under the action of SA during the hydrothermal process, and thus, more Si–O⁻ active groups are generated. The SA molecules were loaded on the composite by absorbing on APT or entering the pores owing to a match of polarity and pore structure. In addition, the bands located at about 1031 cm⁻¹ (corresponding to the Si–O–Si stretching vibration) exhibit negligible changes, which indicates the retention of the SiO₄ tetrahedron of APT after being modified with SA during the hydrothermal process. This is consistent with the SEM analysis results.

**TG Analysis.** The thermal decomposition behaviors of UAPT and SA(0.2)-APT are tested under the air atmosphere, and the TG curves are presented in Figure 4. As can be seen, a successive steep ladder-like characteristic at the first weight-loss step (at 50–130 °C) and the second weight-loss (at 130–380 °C) step, which could be attributed to the removal of residual surface-adsorbed water/zeolitic water and residual structural water (–OH) bonding at the edge of the APT crystal structure in SA(0.2)-APT. Compared to UAPT, the reduced weight loss may be due to the formation of kaolinite without surface-adsorbed water/zeolitic water; (ii) in the third weight-loss step (at 380–600 °C), the TG curves present a successive steep significantly reduced characteristic with the weight loss of 3.63% for UAPT and 26.10% for SA(0.2)-APT, indicating that organic molecules compounded with APT are decomposed besides the residual structural water from APT. The total weight loss is 12.52% for UAPT and 33.44% for SA(0.2)-APT in the range of 25–800 °C, which gives an information that the weight loss of UAPT is lower than that of SA(0.2)-APT. This further confirms that the intense interaction is generated between SA molecules and APT during the hydrothermal process.

**BET Analysis.** Figure 5 and Table 1 exhibit the variations in the pore texture parameters of the as-prepared APT samples. N₂ adsorption–desorption isotherms (Figure 5a) were measured at 77 K and the textural parameters (Figure 5b) were calculated using the BJH method. As observed, all APT samples display a type II isotherm with an H3 hysteresis loop according to the IUPAC classification. At a lower relative pressure (P/P₀ < 0.60), the adsorption–desorption isotherm curves are almost superposed with lower amounts of N₂ adsorbed. This result indicates the existence of a small amount of micropores in the samples. As the relative pressure increases (P/P₀ > 0.80), the amount of N₂ adsorbed increases significantly due to the existence of mesopores (and/or macropores). It can be concluded that the samples possessed narrow slit-like pores or aggregates of plate-like particles. The N₂ adsorption quantity for UAPT at a relative pressure above 0.6 is higher than that for the modified APT samples, which suggests that UAPT possessed a relatively wider PSD with more mesopores or macropores as compared to its modified counterparts.

Two key changes in the PSD in the samples are observed (Figure 5b): (i) the peaks located at 2.568 and 3.743 nm for UAPT, SA(0.01)-APT, and SA(0.05)-APT are attributed to the tight stacking of APT particles and (ii) the peaks located at about 20–35 nm can be ascribed to the aggregation of APT rods. After the modification with 0.2 mol/L SA solution, the PSD of APT at 2.568 nm disappears, and it becomes broader as compared to other samples. Concurrently, the N₂ adsorption quantity of SA(0.2)-APT decreases in the adsorption–desorption isotherm (Figure 5a), which indicates the destruction of the partial pore texture by the high-concentrated SA solution (Table 1). As shown in Table 1, the S₅₇ of the APT samples shows a decreasing trend [130.45 m²/g for UAPT; 97.08 m²/g for SA(0.01)-APT; 89.77 m²/g for SA(0.05)-APT; and 51.15 m²/g for SA(0.2)-APT] as the SA concentration increases but shows a rise (178.24 m²/g) for hydrothermally treated APT (marked as HAPT). This change may possibly be attributed to the removal of dolomite from APT, which facilitates the unclogging of the pore tunnel (it can be proved by XRD analysis). However, it is worth noting that the pore size increases from 14.28 to 14.70 nm and 16.08 nm with increasing SA concentration. After the hydrothermal modification with 0.2 mol/L SA solution, the S₅₇ and PZ of the sample decrease significantly. This observation may be due...
to the reaction between SA and hydroxyl (−OH) groups on the surface of APT, which can clog the pore or tunnel within the crystal.

Zeta Potential. Generally, the composition and charge distribution of APT can be affected by the structural change or the reaction between the surface group and a modifying agent, that is, SA. As observed in Figure 6, the zeta potentials of UAPT, HAPT, SA(0.01)-APT, SA(0.05)-APT, and SA(0.2)-APT are −18.10, −19.00, −26.80, −28.10, and −28.80 mV, respectively. This result indicates that the zeta potential of the sample becomes more negative after modifying with the SA solution. Two main reasons can be provided for this observation: (i) the hydrothermal process can cause the breakage of Si–O–Si and Si–O–M bonds, which in turn results in the partial collapse of the APT crystal structure. As such, more −Si=O− groups may be generated in this process. (ii) Carboxyl functional groups on the surface of APT can generate more negative charges. It is proven that the functionalization of APT with SA via the hydrothermal process is more effective in altering the surface groups and charges. Such an observation is also revealed in the FESEM images (whereby a negligible change in the length of the APT rod is observed).

Adsorption Capacities. Effects of SA Concentration on the Adsorption Capacity. The effects of SA concentration on the MB adsorption capacity of APT are shown in Figure 7a. It can be observed that the adsorption capacity of APT increases significantly with increasing SA concentration. The MB adsorption capacity of APT after being modified with 0.2 mol/L SA solution increases rapidly to 122 mg/g, while that of UAPT is only 46 mg/g. No obvious enhancement to the adsorption capacity can be observed with further increase in the SA concentration [as indicated by the relatively similar adsorption capacities between SA(0.2)-APT and SA(0.3)-APT]. Thus, 0.2 mol/L SA solution is selected as the optimal concentration. The enhanced MB adsorption by the modified APT may be attributed to the carboxyl functional groups. According to Figure 6, the zeta potential of SA(0.2)-APT is more negative than that of UAPT, which indicates the attachment of the C=O group on the surface of APT. As such, this C=O group attachment on the surface of APT may contribute to the enhancement of the adsorption capacity. Furthermore, the enhanced MB adsorption may also arise from the contribution of APT. Based on Figure 2, there is a slight reduction in the length of the rod-like APT crystal after the hydrothermal modification. This causes the breakage of Si–O–Si and Si–O–M bonds, and this subsequently generates more −Si=O− groups in the material, which is favorable for MB adsorption.

Figure 7b shows the effects of the solid/liquid ratio on the MB adsorption capacity of APT. It is clearly observed that there is a sharp increase in the adsorption capacity of APT from 46 mg/g (for UAPT) to 139 mg/g (for SA-APT) after being modified with a solid/liquid ratio of 1/200. This result

Table 1. Microstructural Parameters of APT before and after Modification

| samples      | $S_{\text{BET}}$ (m$^2$/g) | $S_{\text{micro}}$ (m$^2$/g) | $S_{\text{ext}}$ (m$^2$/g) | $V_{\text{total}}$ (cm$^3$/g) | $V_{\text{micro}}$ (cm$^3$/g) | $PZ$/nm |
|--------------|-----------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|--------|
| UAPT         | 130.45                      | 7.36                         | 123.09                      | 0.5094                      | 0.0029                      | 14.28  |
| HAPT         | 178.24                      | 56.58                        | 121.65                      | 0.3036                      | 0.0248                      | 16.88  |
| SA(0.01)-APT | 97.08                       | 6.04                         | 91.04                       | 0.3227                      | 0.0025                      | 14.70  |
| SA(0.05)-APT | 89.77                       | 5.68                         | 84.09                       | 0.3318                      | 0.0023                      | 16.08  |
| SA(0.2)-APT  | 51.15                       | 3.78                         | 47.37                       | 0.1894                      | 0.0016                      | 15.32  |

Figure 5. Nitrogen adsorption−desorption isotherms (a) and pore diameter distribution curves (b).

Figure 6. Zeta potentials of UAPT, HAPT, and SA-APT (prepared with various SA concentrations).
indicates that the solid/liquid ratio used during the preparation process can greatly influence the adsorption capacity of APT. Hence, based on this result, hydrothermally modified APT can be utilized as a high-efficiency adsorbent for the removal of cationic dyes.

**Effects of External pH on the Adsorption Capacity.** Figure 8 exhibits the effects of external pH on the MB adsorption capacity of APT. At a pH of 4, there is a significant increase in the adsorption capacity for SA(0.2)-APT, after which SA-APT demonstrates a relatively constant adsorption capacity with increasing pH values, that is, from 4 to 10. At a low pH of 2, $\text{Si}^-$ and surface $\text{COO}^-$ groups exist in the form of $\text{SiOH}$ and $\text{COOH}$. This results in the hydrogen bonding between MB and APT, which can be considered as the main interaction during the adsorption process. Therefore, the adsorption capacity could obviously decrease. However, at higher pH values, $\text{SiOH}$ and surface $\text{COOH}$ groups will revert back to $\text{SiO}^-$ and $\text{COO}^-$, and this results in the electrostatic forces between MB and APT becoming the dominating interaction during the adsorption process. It is worth noting that the electrostatic force is much stronger than hydrogen bonding, and the switching from hydrogen bonding to electrostatic force with increasing pH is beneficial to the adsorption of cationic dye MB by APT. As the pH value increases further, the number of negatively charged groups in APT, that is, $\text{SiO}^-$ and $\text{COO}^-$, increases, and this allows more cationic MB dye to be adsorbed onto the surface of APT. Thus, it can be concluded that the electrostatic interaction is dominant during the adsorption process. As discussed earlier, the specific surface area of the hydrothermally modified APT is smaller than that of UAPT, and the specific surface area decreases from 130.45 (UAPT) to 51.15 (SA(0.2)-APT) $\text{m}^2/\text{g}$. However, based on Figure 8, the adsorption capacity of UAPT is significantly lower than that of SA(0.2)-APT, which suggests that the specific surface area is not the primary influencing factor.
factor for the adsorption of MB. Hence, it is worth noting that the specific surface area of APT exerts smaller effects on the adsorption capacity when compared to the type of dominating interaction during the adsorption process.

**Effects of Contact Duration on the Adsorption Quantity.** Research on the effects of contact duration on adsorption quantity may be conducive toward providing meaningful data for the understanding of adsorption process characteristics. Figure 9a shows the influence of contact duration on the quantity of MB adsorbed by APT samples. As observed, the adsorption of MB by APT is a fast process, and adsorption equilibrium can be nearly achieved within 20 and 60 min for SA(0.2)-APT and UAPT, respectively. To further investigate the equilibrium, a fast process, and adsorption quantity of MB adsorbed by APT samples. As observed, the adsorption of MB by APT is a fast process, and adsorption equilibrium can be nearly achieved within 20 and 60 min for SA(0.2)-APT and UAPT, respectively. To further investigate the dynamic adsorption behaviors between the adsorbent and MB, the adsorption data were analyzed with both pseudo-first-order (eq 2) and pseudo-second-order (eq 3) kinetic models.

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

(2)

\[
t/q_t = 1/(k_2 q_e^2) + t/q_e
\]  

(3)

where \(k_1 (\text{min}^{-1})\) and \(k_2 (\text{g/mg}\cdot\text{min})\) are the rate constants calculated from pseudo-first-order and pseudo-second-order kinetic models, respectively. \(k_1\) can be determined from the intercept of \(\ln(q_e - q_t)\) versus \(t\) line, while \(k_2\) can be determined from the slope of \(1/q_t\) versus \(t\) line. \(q_t (\text{mg/g})\) and \(q_e (\text{mg/g}^{-1})\) are the amounts of dye adsorbed per unit mass of adsorbent at any time \(t\) (s) and at equilibrium, respectively. The corresponding curves are shown in Figure 9b, c, and the corresponding parameters are presented in Table S1. The fitted data based on the pseudo-second-order model for UAPT and SA(0.2)-APT show good linear relationships with good correlation coefficients of \(R^2 = 0.9989\) and 0.9994, respectively. However, the linear correlation coefficients obtained from the fitted curves based on the pseudo-first-order kinetic model are very low, that is, \(R^2 = 0.6216\) (UPAT) and 0.6110 (SA-APT). Concurrently, the experimental data are almost consistent with the \(q_{e,2}\) value theoretically obtained from the pseudo-second-order model. However, the calculated \(q_{e,2}\) value based on the pseudo-first-order model is entirely different from that obtained in the experiment (see Table S2). Thus, the pseudo-second-order kinetic model may be more suitable than the pseudo-first-order kinetic model in describing the MB adsorption behaviors of UAPT and SA-APT. The interaction between the adsorbent and adsorbate is more inclined to the associated chemisorption and the surface diffusion process, and electrostatic interaction and interior complexing adsorption are the main driving force for the adsorption process.

**Effects of Initial Concentration and Adsorption Isotherms on the Adsorption Capacity.** Figure 10a shows the effects of initial MB concentration on the adsorption capacities of UAPT and SA-APT. According to the result, the adsorption capacities of the adsorbents increase rapidly with increasing initial MB concentration. This result illustrates the improvement in the driving force at the solid—liquid interface with increasing initial MB concentration, before the adsorption sites are saturated with MB. An adsorption capacity equilibrium can be observed at MB concentrations higher than 200 mg/L for UAPT and SA-APT, which indicates the saturation of the available adsorption sites by MB. To study the adsorption mechanism of adsorbents on dye molecules, Freundlich and Langmuir isotherm models have been frequently used. The Freundlich and Langmuir equations are shown as follows:

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e
\]  

(4)

\[
\frac{q_e}{q_m} = \frac{1}{a_m b} + \frac{c_e}{q_m}
\]  

(5)

where \(Q_e (\text{mg/g}^{-1})\) is the MB adsorption capacity of APT at equilibrium and \(C_e (\text{mg/L})\) is the MB concentration after equilibrium. \(a_m\) is the saturated adsorption capacity (mg g\(^{-1}\)) and \(b\) (L mg\(^{-1}\)) is the Langmuir constant, which is in relation to the adsorption energy. \(K_F\) [(mg g\(^{-1}\)/(L mg\(^{-1}\))] and \(n\) are the Freundlich constant and adsorption intensity, respectively. Equilibrium adsorption parameters were calculated from the linear fitting equations based on the Langmuir and Freundlich isotherm models (Figure 10b, c), and they are summarized in Table S3 (Supporting Information). Based on the results, the linear correlation coefficients \(R^2\) based on the Langmuir isotherm model for SA-APT and UAPT are 0.9992 and 0.9942, respectively. Such results are better than those calculated using the Freundlich isotherm model \((R^2 = 0.8949\) for SA-APT and \(R^2 = 0.8614\) for UAPT). Furthermore, the experimental adsorption capacity \((q_m)\) is 207.84 mg/g, while \(q_{m0}\) which is theoretically calculated from the Langmuir isotherm model, is 227.27 mg/g. Both the experimentally obtained value and theoretically obtained value are relatively close, which suggests that the adsorption process complies with the Langmuir model instead of the Freundlich model. Also, since \(1/n\) is smaller than 1, this suggests that the MB adsorption on APT is akin to the monolayer adsorption. Based on the abovementioned results, all adsorption sites on the adsorbent are identical and the
monolayer adsorption only occurs on the surface rather than the immigration of adsorbate in the plane of the surface according to the Langmuir isotherm.\textsuperscript{49} SA-APT exhibits the optimal adsorption capacity, which is significantly higher than that exhibited by UAPT. This result confirms that the generation of more adsorption sites on APT after the hydrothermal modification can facilitate the removal of a cationic dye.

Figure 11 shows the MB removal ratio by UAPT, HAPT (attapulgite was hydrothermally treated in water as the solvent), and SA-APT at an initial MB concentration of 150 mg/L. As shown in the result, the MB removal ratio by SA-APT (99.7%) is much higher than that by UAPT (35.0%). However, it is worth noting that the MB removal ratio by HAPT is only 62.7%, which indicates that the hydrothermal process may have a slight effect on the adsorption capability of the material. Such a result indicates that the MB removal efficiency exhibited by SA-APT is mainly due to the hydrothermal process-assisted modification. SA-APT is almost able to completely remove MB in a 150 mg/L MB solution, and such a performance is valuable in the practical application.

**Adsorption Mechanism.** To elucidate the adsorption mechanism, FTIR spectra of the adsorbent before and after adsorption were measured. As shown in Figure 12a, the bands located at about 3615, 3690 (Mg/Al/Fe)O−H, and 3548 cm\(^{-1}\) (Si)O−H for SA-APT-MB are significantly weakened. For UAPT-MB, the band located at about 1652 cm\(^{-1}\) (hydroxyl groups) is slightly weakened. However, the same band almost disappeared for SA-APT-MB materials. These results confirm that the H-bonding interaction between APT and MB can be formed, and this leads to the improvement in the adsorption capability of the material. Based on Figure 12, new absorption bands located at about 1593, 1389, and 1333 cm\(^{-1}\) appear after the MB adsorption process, which can be attributed to the stretching vibrations of C=S and C−N bonds in MB.\textsuperscript{52−54} All the abovementioned peaks for SA-APT-MB are much stronger than those for UAPT-MB, which suggests that more adsorption sites can be generated on the surface of SA-APT than UAPT. As a result, more MB molecules can be adsorbed on the surface of SA-APT during the adsorption process as compared to that on UAPT. Furthermore, modified SA-APT is also negatively charged in the aqueous SA solution due to the presence of −COO\(^{-}\) groups (as shown in the zeta potential results). This can significantly increase the formation of −Si−O− groups (due to the breakage of Si−O−Si and Si−O−M bonds) and −COO\(^{-}\) groups, which can strengthen the electrostatic interaction between the adsorbent and adsorbate. Also, new complexing or association interactions between SA-APT and MB may be generated. In contrast, the adsorption mechanism in UAPT is largely based on the weaker electrostatic attraction between the low-charge-density surface of UAPT and MB and the hydrogen-bonding interaction between Si−OH and the C−N moiety in MB. As discussed earlier, the possible MB adsorption mechanism in SA-APT is illustrated in Figure 12b.

**CONCLUSIONS**

APT was functionalized successfully via a hydrothermal process in this work, whereby enhanced MB adsorption capacity by the modified APT was achieved. Based on the results, it was shown that (i) dolomite was removed during the hydrothermal process along with the increase in the quantity of the pore adsorption site; (ii) the inner Si−O−Si and Si−O−M bonds in the APT crystal framework could be broken during the hydrothermal process, and this led to the generation of more active adsorption sites; and (iii) SA was successfully introduced to generate more −COO\(^{-}\) groups on the surface of APT to provide more adsorption sites. It was shown that increasing the negative charges on the surface of SA-APT could result in the adsorption of more cationic MB dye molecules. After the hydrothermal modification, the rod-shaped APT became shorter as compared to its unmodified counterpart.

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**Figure 11.** Comparison of the MB removal by UAPT, HAPT, and SA-APT at an initial MB concentration of 150 mg/L (inset showing the photographic images of various systems at the end of the experiment). Photograph courtesy of “Zhifang Zhang”. Copyright 2020.

**Figure 12.** (a) FTIR spectra of MB, UAPT-MB, and SA-APT-MB; (b) possible adsorption mechanism between SA-APT and MB.
The BET specific surface area of SA(0.2)-APT was significantly lower than that of UAPT, which could be due to the partial collapse of the pore structure. Even though SA(0.2)-APT possessed a lower specific area, it was still able to exhibit a superior adsorption capacity than UAPT. This result indicates that the specific surface area of a material is not the dominant factor in determining the adsorption efficiency. Instead, more emphasis should be placed on the type of interactions between the adsorbent and adsorbate, for example, hydrogen bonding, electrostatic, and complexing. The modified APT could remove MB completely at an initial MB concentration of 150 mg/L, which greatly exceeded that exhibited by the unmodified APT. This approach can provide a facile, scalable, and sustainable method for the preparation of a functionalized APT adsorbent by using low-cost and contaminant-free SA as the modifier. Hence, the functionalized APT adsorbents were able to exhibit a better adsorption capacity and a higher MB removal efficiency. Such an approach can also provide a facile, effective, and sustainable strategy to address the water pollution issues.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02111.

Surface distribution of the C element in APT before and after the hydrothermal modification: (a) UAPT, (b) SA(0.01)-APT, (c) SA(0.05)-APT, and (d) SA(0.2)-APT; surface distribution of the O element in APT before and after the hydrothermal modification: (a) UAPT, (b) SA(0.01)-APT, (c) SA(0.05)-APT, and (d) SA(0.2)-APT; element content of UAPT and SA(0.2)-APT samples; adsorption kinetic parameters of UAPT and SA-APT for MB; and isotherm parameters for the adsorption of MB onto SA-APT (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the National Natural Science Foundation of China (grant no. 32002136) for the financial support of this research. The authors would also like to thank the scientific research start-up funds for openly recruited doctors (no. 2017RCZX-40) and the open funds of Key Laboratory of Clay Mineral Applied Research of Gansu Province (no.: CMAR-2019-4).

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