ABSTRACT: Using N-isopropylacrylamide (NIPAM) and acrylic acid (AAc) as monomers, N,N'-methylenebisacrylamide (MBA) as a cross-linking agent, and molybdenum disulfide (MoS2) as functional particles, a P(NIPAM-co-AAc)/MoS2 composite hydrogel was prepared by free radical polymerization initiated by ultraviolet light. The results of Fourier transform infrared spectroscopy, Raman spectroscopy, and scanning electron microscopy show that MoS2 has been successfully introduced into the P(NIPAM-co-AAc) system, and the obtained composite hydrogel has a porous network structure. Studies on the swelling property and dye adsorption performance show that the addition of MoS2 can increase the swelling ratio of P(NIPAM-co-AAc) hydrogels to a certain extent and can significantly improve the ability of the P(NIPAM-co-AAc) hydrogel to adsorb methylene blue (MB). The adsorption process of MB by the composite hydrogels conforms to the pseudo-second-order kinetics and the Langmuir isotherm adsorption models. The estimated equilibrium adsorption capacity (Q_m) using the Langmuir isotherm model can reach 1258 mg/g, mainly due to the electrostatic interaction between the negatively charged groups −COO− and MoS2 particles on the network structure and the positively charged dye MB. The adsorption of MB by P(NIPAM-co-AAc)/MoS2 composite hydrogels depends on the temperature during adsorption. Compared with room temperature, a high temperature of 40 °C above the poly(N-isopropylacrylamide) (PNIPAM) phase transition temperature (∼32 °C) leads to a decreased adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel for MB due to the enhanced hydrophobic properties of the network structure and the decrease of the swelling ratio. The prepared hydrogel material can be used as a good adsorbent for dyes, which is promising in wastewater treatment.

INTRODUCTION

The discharge of dye-containing wastewater in various countries in the world is increasing. Once the water body is polluted, it is not easy to restore to the expected original state quickly. At present, adsorption technology is considered by environmental researchers to be the most effective and promising method for sewage treatment. Therefore, it is essential to develop an economical and efficient material for adsorbing harmful substances. The adsorption materials that have been reported are organic and inorganic materials, including poly(4,4′-diaminodiphenylmethane), polyelectrolyte multilayers, polyaniline and polypyrrole macro-/nanoparticles, sodium titanate, CoMo4, sandwichlike magnesium silicate/reduced graphene oxide nanocomposite, activated carbon, and carbon nanotubes. However, the adsorption materials that have been reported so far also have many shortcomings, such as complex preparation processes, use of toxic and hazardous substances, poor stability, and weak adsorption capacity.

Hydrogel is a polymer network with a three-dimensional structure that is porous and has a large surface area and many channels. Because of the presence of hydrophilic groups such as hydroxyl, carboxylic acid, amide, and sulfonic acid groups in the polymer forming the hydrogel structure, the hydrogel has an affinity for water, swells in water but does not dissolve, and can absorb a large amount of water. Poly(N-isopropylacrylamide) (PNIPAM) hydrogels are temperature-sensitive and are a type of intelligent hydrogels that have been studied extensively. The temperature response is corresponding to a discontinuous volume phase change, which can be found near 32 °C. Copolymerization of NIPAM and acrylic acid (AAc) can lead to a copolymer P(NIPAM-co-AAc), which can form a chelate with various metal ions to achieve good adsorption performance due to the presence of the AAc units containing...
ionizable and hydrophilic carboxyl groups and its function as an excellent chelating group. The obtained composite hydrogel can have better swelling, adsorption, pH response, and other properties.15 For example, Kureha et al.21 studied the structural changes of P(NIPAM-co-AAc) microgels and found that the hydrophobic and electrostatic interactions between cationic dye molecules and anionic microgels affected the separation of microgels and phase transition behavior. Compared with other adsorption materials, the hydrogel has good biocompatibility, environmental friendliness, higher adsorption rate, adsorption capacity, and is easy to prepare. As a fast response and high-capacity adsorption material, the hydrogel has become an important material for removing heavy metals,22,23 herbicides,24 organic dyes,25 and many other pollutants from aqueous media.

The hydrogel has a large surface area and numerous channels inside, providing adsorption sites, and can be used as an ideal material for adsorbing dye molecules. However, a single hydrogel has low strength and low adsorption capacity. Introducing functional components,26 loading with a certain amount of inorganic nanoparticles,27,28 and designing a double cross-linked network structure29 can greatly improve the mechanical properties, adsorption capacity, environmental stimulus–response performance, and stability of the hydrogels.30–35 Inorganic nanoparticles have unique properties in mechanical, electrical, magnetic, thermal, optical, and chemical activities due to their unique volume effect, surface effect, quantum size effect, and macroscopic quantum tunneling effect. Recently, with the development of nanoscience and nanotechnology, nanomaterials have great potential to solve environmental problems.36–38 Compared with traditional materials, nanostructured materials have a higher surface area and show higher adsorption efficiency and faster adsorption rate in water treatment. In addition, nanomaterials also have the following characteristics: they have high adsorption performance, are not harmful to the environment, and can be easily recycled from the environment. In the hydrogel system, the introduction of nanomaterials, including graphene oxide,39,40 Fe3O4,41,42 manganese oxide (MnO2),43 titanium oxide (TiO2),44,45 and zinc oxide (ZnO),46 to prepare composite hydrogels plays an increasingly important role in the wastewater treatment process. Nanomaterials can be successfully used as efficient, economical, and environmentally friendly adsorbents to remove various toxic substrates in wastewater, such as heavy metals and azo dyes. Zhao et al.47 prepared a three-dimensional hemin-functionalized graphene hydrogel (Hem/GH) by a simple self-assembly method, which showed good mechanical strength and a high adsorption capacity of 341 mg g−1 for rhodamine B (RhB). The above-reported research work provides a new way for preparing hydrogel materials with high dye adsorption capacity and excellent mechanical properties. However, it is still necessary to explore new inorganic nanomaterials to prepare composite hydrogels with low cost and high adsorption capacity, which is helpful for sewage purification and environmental protection.

![Figure 1](https://pubs.acs.org/acsomegajournal/acsomegajournal-2021-00000030.png)
Two-dimensional layered molybdenum disulphide (MoS₂) is composed of a single layer or a few layers of MoS₂. It is a two-dimensional nanomaterial with a sheet structure similar to the carbon material graphene. It has become a research hotspot in the field of emerging materials due to its excellent optoelectronic properties. Schneider et al. prepared poly(lactic acid) (PLA) by solution blow spinning (SBS) technology and then modified by spraying with MoS₂ to obtain the PLA/MoS₂ nanocomposite. The results show that the MoS₂ nanoflakes used to alter the sub-micrometer fibers achieve an adsorption capacity of 111.2 mg g⁻¹ for methylene blue (MB). The high adsorption capacity of MoS₂ combined with the interconnected pores of the fiber membrane and simple modification strategies make PLA/MoS₂ fiber composite materials particularly suitable for high-performance adsorption membranes. This study by Tian et al. shows that the use of MoS₂/CuS nanosheet composites (NCs) as adsorbents can quickly and effectively remove different dyes in wastewater. MoS₂/CuS NCs are prepared by a simple hydrothermal route. The adsorption capacity of the composite material for rhodamine B (RhB), methylene blue (MB), methyl orange (MO), and rhodamine 6G dyes (RhB 6G) is 273.23, 432.68, 98.78, and 211.18 mg/g, respectively. This is due to its high specific surface area (106.27 m²/g) and small mesopores (2.3 nm), providing numerous adsorption sites and uniform coverage for dye molecules. Based on the unique volume effect and surface effect of nanomaterials, when nanoparticles are introduced into the hydrogel to form composite materials, the nanoparticles can maintain their original characteristics and adjust the physical and chemical properties of the nanocomposite hydrogel materials in a variety of ways. For example, changing the amount of nanoparticles can make the comprehensive performance of the nanocomposite better than each single component and even obtain some new properties to meet the application requirements of high-capacity dye adsorption.

In this study, the P(NIPAM-co-AAc)/MoS₂ composite hydrogel was prepared by free radical polymerization of NIPAM and AAc initiated by ultraviolet light. The influence of adsorption temperature, MoS₂ loading content, and other factors on the structure and performance of hydrogels was studied. The synthesis of the composite hydrogel containing MoS₂ is simple, its adsorption capacity for MB is high, and it can be more effectively used in water treatment for the removal of dyes.

**RESULTS AND DISCUSSION**

Figure 1 shows the formation reaction process of the P(NIPAM-co-AAc)/MoS₂ composite hydrogel prepared in this work: the temperature phase transition of the hydrogel, the dye adsorption behavior of the hydrogels, and the appearance of the prepared hydrogels. As shown in Figure 1a, NIPAM and AAc were used as monomers, and the photoinitiator 2960 was used to initiate the polymerization and cross-linking reaction of the monomers by ultraviolet light irradiation. In the presence of MoS₂ particles, the P(NIPAM-co-AAc)/MoS₂ composite hydrogel was obtained. The introduction of the NIPAM unit endows the composite hydrogel with temperature-responsive properties. The effects of different temperatures on the three-dimensional cross-linked network structure and swelling and shrinkage properties of the composite hydrogel can be studied. As shown in Figure 1b, the composite hydrogel undergoes a volume phase transition at 40 °C above the phase transition temperature. Because AAc contains a carboxylic group, it has a negative charge and can interact with positively charged dye molecules in water in the next step. MoS₂ particles are a kind of flake-shaped granular material, which can take advantage of its superior size and surface effect and combine with AAc to improve the adsorption capacity of dyes. Figure 1c shows the dye adsorption behavior at room temperature and 40 °C.

By controlling the content of MoS₂ inorganic particles, five groups of hydrogels were prepared by free radical copolymerization in this experiment. Table 1 shows the formula and product information of the P(NIPAM-co-AAc)/MoS₂ composite hydrogels, and their appearance is shown in Figure 1d. Among them, NG-1 is the blank control sample P(NIPAM-co-AAc) hydrogel without added MoS₂. In addition, NG-2, NG-3, NG-4, and NG-5 are P(NIPAM-co-AAc)/MoS₂ composite hydrogels with different MoS₂ loading amounts, including 1, 5, 10, and 25 mg, accounting for 0.1, 0.5, 1, and 2.5% of the NIPAM content, respectively. It can be seen from Table 1 and Figure 1d that the appearance of the hydrogel without added MoS₂ in NG-1 is white. As the amount of added MoS₂ increases, the color of the prepared hydrogel becomes darker and gradually turns black from gray. This is because as MoS₂ particles appear black, they make the hydrogel appear black. In the next step, a series of tests and characterization will be conducted on the synthesized hydrogel to study its composition, swelling, and dye adsorption properties.

Figure 2 shows Fourier transform infrared (FT-IR) and Raman spectra of P(NIPAM-co-AAc) and P(NIPAM-co-AAc)/MoS₂ composite hydrogels. As seen in Figure 2a, there are two strong absorbance bands located at 3440 and 1640 cm⁻¹, corresponding to the stretching vibration of OH in AAc and NH in NIPAM, and the stretching vibration of C=O in AAc and NIPAM, respectively. The characteristic absorbance of the two peaks at 1380 and 1108 cm⁻¹ is assigned to the stretching vibration of CO in AAc, indicating that the composite hydrogel containing monomer units including NIPAM and AAc was successfully synthesized. According to the infrared spectra of P(NIPAM-co-AAc)/MoS₂ composite hydrogels with different contents of MoS₂, it can be seen that the characteristic absorbance bands of the P(NIPAM-co-AAc) hydrogel also appears at around 3437 and 1636 cm⁻¹. Since the FT-IR spectra were usually used for qualitative analysis, it is impossible to confirm whether there is any introduction of inorganic MoS₂ particles in the P(NIPAM-co-AAc) hydrogel. Therefore, in the following analysis, Raman spectroscopy was used to determine the presence of MoS₂.

Figure 2b shows the Raman spectra of MoS₂, P(NIPAM-co-AAc) hydrogels, and P(NIPAM-co-AAc)/MoS₂ composite hydrogels. In the Raman spectrum of MoS₂, it was found that there are two strong characteristic peaks at about 403 and 374 cm⁻¹, which are attributed to the out-of-plane vibration.
In the Raman spectrum of the P(NIPAM-co-AAc) hydrogel without MoS$_2$, a wide band was found at 1000−2000 cm$^{-1}$, indicating the amorphous dried hydrogel, and no MoS$_2$ characteristic peak was found. When the MoS$_2$ loading content is low, there are rather weak peaks belonging to MoS$_2$ in the Raman spectrum of P(NIPAM-co-AAc)/MoS$_2$. When the MoS$_2$ content reaches more than 10 mg, the characteristic peak of MoS$_2$ appears, indicating that MoS$_2$ has been successfully incorporated into the P(NIPAM-co-AAc) hydrogel. As seen in Figure 2b, compared to NG-4, NG-5 with a higher MoS$_2$ content should have an increased intensity of the characteristic Raman absorbance bands. However, the intensity of the characteristic MoS$_2$ peaks at about 403 and 374 cm$^{-1}$ in NG-5 was slightly lower than that in NG-4. It is most likely that at a very high concentration (2.5%) of MoS$_2$ dispersion during the preparation of NG-5, the inorganic MoS$_2$ particles are becoming unstable and prone to form aggregates, resulting in an uneven composition of the P(NIPAM-co-AAc)/MoS$_2$ composite hydrogels. At a lower MoS$_2$ content, because the hydrogel encapsulates and shields MoS$_2$, the characteristic peaks of MoS$_2$ are not obvious in the spectrum.

Thermogravimetric analysis (TGA) should be used for detecting the MoS$_2$ content in the P(NIPAM-co-AAc)/MoS$_2$ composite hydrogels. Figure S1a shows the TGA curves of P(NIPAM-co-AAc) and P(NIPAM-co-AAc)/MoS$_2$ composite hydrogels. Figure S1b shows an enlarged part of the indicated area with a green frame in Figure S1a. From Figure S1, it can be seen that the char residual mass ratio of the pure P(NIPAM-co-AAc) hydrogel NG-1 is about 5.54%. The char residual mass ratio of P(NIPAM-co-AAc)/MoS$_2$ composite hydrogels including NG-3, NG-4, and NG-5 are 5.97, 6.61, and 8.11%, respectively. The MoS$_2$ contents of NG-3, NG-4, and NG-5 were calculated to be 0.43, 1.07, and 2.57%, respectively.
The calculated values are very consistent with the theoretical values. Figure 3a shows the scanning electron microscope (SEM) image of MoS$_2$ particles. It can be seen from Figure 3a that MoS$_2$ exists in the form of flakes. Through statistical average, the average size of the flake diameter of MoS$_2$ is about 3.2 $\mu$m. Using transmission electron microscope (TEM) to analyze the single irregularly shaped particle of MoS$_2$ (see Figure 3b), the size of the MoS$_2$ flake is about 3.4 $\mu$m. Figure 3c shows the $\zeta$-potential distribution of MoS$_2$ particles. The $\zeta$-potential of particles is considered to be an important parameter for characterizing the stability of the colloidal dispersions and gives information on the effective surface charge. As shown in Figure 3c, it can be seen that the $\zeta$-potential of MoS$_2$ particles is about $-27.5$ mV, indicating that the dispersion is relatively stable and the electrostatic force is large. Since MoS$_2$ is negatively charged, it is beneficial to adsorb oppositely charged dye molecules through an electrostatic force.

Figure 4 shows the swelling ratio of the P(NIPAM-co-AAc) hydrogel and the P(NIPAM-co-AAc)/MoS$_2$ composite hydrogel as a function of time (a), and the equilibrium swelling ratio of hydrogels as a function of the MoS$_2$ loading content (b). Figure 5 shows the dye adsorption capacity of P(NIPAM-co-AAc)/MoS$_2$ and P(NIPAM-co-AAc) hydrogels as a function of time at room temperature (a) and 40 °C (b); (c) appearance of the hydrogels before and after adsorption; and (d) adsorption curve of MB by the composite hydrogel and the adsorption kinetic models at room temperature.
the equilibrium swelling ratio and the amount of MoS₂ added. As shown in Figure 4a, the swelling ratio of the P(NIPAM-co-AAc) hydrogel without MoS₂ is first increased with time from 0 to 12 h. It then changes slowly after 12 h, and the final swelling ratio reaches about 95 g/g. The P(NIPAM-co-AAc)/MoS₂ composite hydrogel obtained after the addition of MoS₂ shows a similar change trend. The final equilibrium swelling ratio is higher than that of the pure P(NIPAM-co-AAc) hydrogel. Figure 4b shows the relationship curve between the equilibrium swelling ratio of P(NIPAM-co-AAc)/MoS₂ composite hydrogels and the amount of the added MoS₂. It can be seen that the equilibrium swelling ratio began to increase sharply with the increase of the amount of MoS₂ and tended to be stable when the amount of addition was 10 and 25 mg. When 25 mg is added, the equilibrium swelling ratio of the P(NIPAM-co-AAc)/MoS₂ composite hydrogel can reach 176.5 g/g. This is mainly because MoS₂ itself has oxygen-containing groups on the surface and is negatively charged. As the amount of the added MoS₂ increases, the hydrophilicity of the composite hydrogel improves, leading to the expansion of the networks. At the same time, because MoS₂ itself is negatively charged, the increase of MoS₂ caused the electrostatic repulsion of the same charged counterparts in the network structure, resulting in an increase in the volume and swelling ratio. The excellent swelling performance indicates that the composite hydrogel may have a high dye adsorption capacity.

Figure 5 shows the relationship between the amount of dye adsorption of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels as a function of time at room temperature and 40 °C, as well as the appearance of the hydrogel before and after adsorption, and the adsorption kinetic models of MB by the hydrogel. Note that the initial concentration of MB for the adsorption experiment is 64 mg/L. It can be seen from Figure 5b that with the increase of time, the adsorption capacity of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels to MB is gradually increased and begins to reach adsorption equilibrium at about 6 h. The adsorption capacity of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels at equilibrium is 91 and 35 mg/g, respectively. By comparing the results from Figure 5a,b, the adsorption temperature greatly influences the adsorption capacity of both hydrogels. With the increase of the adsorption temperature, when the dye adsorption is performed above the phase transition temperature near 32 °C, the adsorption capacity of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels at equilibrium was both also decreased. This shows that the hydrogel swells in the solution at room temperature, the molecular chain stretches, the three-dimensional porous cross-linked network structure, and numerous channels are beneficial to the diffusion and adsorption of dye molecules. Above the phase transition temperature of 32 °C, the macromolecular chain collapses and water is discharged. The three-dimensional cross-linked network structure shrinks, which is not conducive to the diffusion and adsorption of dye molecules, resulting in lower dye adsorption quantity.

Table 2. Kinetic Parameters for the Adsorption of MB in P(NIPAM-co-AAc) and P(NIPAM-co-AAc)/MoS₂ Hydrogels at Room Temperature

| sample                        | pseudo-first-order constants | pseudo-second-order constants |
|-------------------------------|-------------------------------|-------------------------------|
|                               | qₑ (mg/g) | Kᵣ (min⁻¹) | R²   | qₑ (mg/g) | Kᵣ (g/mg × min) | R²   |
| P(NIPAM-co-AAc)/MoS₂          | 205.5     | 0.354       | 0.963 | 212.5     | 3.503           | 0.982 |

Figure 5c shows the appearance of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels before adsorption. Both freeze-dried samples with the same mass of 10 mg are much smaller. The freeze-dried hydrogel containing MoS₂ is black granules, while the one without MoS₂ is white. After MB dye molecules are adsorbed, the hydrogel volume is much larger than the original one, and the color is blue, indicating that MB dye molecules are absorbed on the surface and bound to the hydrogel. Considering that the P(NIPAM-co-AAc)/MoS₂ composite hydrogel has a high dye adsorption capacity, Figure 5d shows the adsorption kinetics and simulation curves of MB adsorption on the P(NIPAM-co-AAc)/MoS₂ composite hydrogels at room temperature. The experimental data are fitted with two kinetic models, pseudo-first-order and pseudo-second-order models (see eqs 1 and 2).

\[
\frac{dq}{dt} = k₁(qₑ - q₁) \tag{1}
\]

\[
\frac{dq}{dt} = k₂(qₑ - q₁)^2 \tag{2}
\]

where \(qₑ\) and \(q₁\) (mg/g) represent the equilibrium adsorption capacity and the adsorption capacity at contacting time \(t\), and \(k₁\) and \(k₂\) are pseudo-first-order constant and pseudo-second-order constant. Table 2 shows the kinetic parameters for the adsorption of MB in P(NIPAM-co-AAc) and P(NIPAM-co-AAc)/MoS₂ hydrogels at room temperature. From Figure 5d and Table 2, it can be seen that at room temperature, the correlation coefficient value \((R²)\) of the pseudo-second-order
model reaches 0.982, which is higher than that for the pseudo-first-order model. This indicates that the adsorption of MB dye molecules onto P(NIPAM-co-AAc)/MoS₂ composite hydrogels follows the pseudo-second-order model well.

As indicated in the literature, the kinetics of adsorption study in the regions with constant adsorption acceleration (abbreviated as KASRA) model was also used to calculate the kinetics of the adsorption process. According to the KASRA model, the adsorption kinetics curve is composed of two regions (1 and 2). Regions 1 and 2 like regions I and II in adsorption isotherms are belonging to the most active and rest of sites, respectively. Several first data and then remaining data were fitted in a quadratic KASRA equation (see eqs S1–S3 in the Supporting Information). The adsorption kinetic experiment was performed at a MB initial concentration of 64 mg/L. The obtained data were analyzed by the KASRA model, as shown in Figure S1 and Table S1. As shown in Figure S1 and Table S1, the kinetic curves are composed of two regions (1 and 2). Regions 1 and 2 like regions I and II in adsorption isotherms pay to the most active and rest of sites, respectively. We fit several first data and then the remaining data in a quadratic equation. In region 1, the coefficients including $A$, $B$, and $R^2$ of the KASRA equation are calculated to be $-0.613$, $24.12$, and $0.706$, respectively. In region 2, $A$, $B$, $C$, and $R^2$ are estimated to be $-4.28 \times 10^{-3}$, $0.085$, $194.17$, and $0.89$, respectively. As indicated in the results above, the experimental data were fitted with two kinetic models, pseudo-first-order and pseudo-second-order models (see eqs 1 and 2). It can be seen that at room temperature, the correlation coefficient values ($R^2$) of pseudo-second-order and pseudo-first-order models reach 0.982 and 0.963, which are both higher than the two values of 0.706 and 0.890 at 40 °C. This indicates that the adsorption of MB dye molecules onto P(NIPAM-co-AAc)/MoS₂ composite hydrogels follows the pseudo-second-order model well.

Figure 6a,b shows the adsorption isotherms of P(NIPAM-co-AAc)/MoS₂ and P(NIPAM-co-AAc) hydrogels for MB at room temperature and 40 °C. Figure 6c indicates the plotting curves of Langmuir and Freundlich isotherm adsorption models (c) and the ARIAN model (d) for the MB adsorption of P(NIPAM-co-AAc)/MoS₂ at room temperature.
Large specific surface area, and is negatively charged, which can adsorb a large amount of MB through the electrostatic attraction and van der Waals forces. This shows that the addition of MoS2 can improve the adsorption performance of the pure P(NIPAM-co-AAc) hydrogel. The adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel can reach 916 mg/g when the MB initial concentration is 640 mg/L.

It can be seen from Figure 6b that at 40 °C, the adsorption capacity of P(NIPAM-co-AAc)/MoS2 and P(NIPAM-co-AAc) hydrogels show a trend similar to that at room temperature with the increase of the MB concentration. Compared to room temperature, the increased adsorption temperature of 40 °C leads to the decreased adsorption capacity of P(NIPAM-co-AAc)/MoS2 and P(NIPAM-co-AAc) hydrogels at different concentrations. This is because the PNI-PAM hydrogel is temperature-sensitive and has a characteristic phase transition temperature. At the adsorption temperature of 40 °C above the phase transition temperature (32 °C), the volume of hydrogels shrinks sharply. At room temperature, water molecules interact strongly with amide groups through hydrogen bonds, resulting in the PNI-PAM hydrogels having a good affinity with water molecules. When the temperature is higher than the phase transition temperature, the hydrogen bonds between water molecules and amide groups are destroyed, and the hydrophilic force is weakened. The polymer chains are collapsed, and the volume of hydrogels shrinks significantly. At the same time, the chance of MB entering the hydrogel is reduced, and the amount of MB binding with the hydrogel is decreased. Therefore, as the temperature increases, the adsorption capacity of P(NIPAM-co-AAc)/MoS2 and P(NIPAM-co-AAc) hydrogels are both reduced. When the initial concentration of MB is 640 mg/L, the adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel decreases from 916 to 620 mg/g, and the adsorption capacity of the P(NIPAM-co-AAc) hydrogel is reduced from 598 to 402 mg/g.

Figure 6c shows the plotting curves of Langmuir and Freundlich isotherm adsorption models for the MB adsorption of P(NIPAM-co-AAc)/MoS2 at room temperature. As shown in Figure 6c, as the equilibrium concentration of MB increases, the equilibrium adsorption capacity of the P(NIPAM-co-AAc) hydrogel increases. Langmuir (eq 3) and Freundlich (eq 4) isotherm models were used to evaluate the relationship between the equilibrium adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel for MB and the equilibrium MB concentration.

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)
\]

\[
q_e = K_F C_e^{1/n} \quad (4)
\]

where \( q_m \) (mg/g), 1/n, \( q_e \) (mg/g), \( C_e \) (mg/L), \( K_L \) (L/mg), and \( K_F \) (mg/g) represent maximum adsorption capacity, adsorption intensity, adsorption capacity, the equilibrium concentration of MB dyes, the Langmuir constant, and the Freundlich constant, respectively. Table 3 shows Langmuir and Freundlich isotherm parameters for the adsorption of MB onto P(NIPAM-co-AAc)/MoS2 hydrogels at room temperature. From Figure 6c and Table 3, it can be seen that the adsorption isotherm of the P(NIPAM-co-AAc)/MoS2 composite hydrogel for MB at room temperature is more consistent with the Langmuir adsorption isotherm model, and \( R^2 = 0.994 \). According to the Langmuir isotherm adsorption model simulation, the maximum adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel can reach 1258 mg/g.

As reported in the literature, the “adsorption isotherm regional analysis model” (abbreviated as ARIAN model) should be used to analyze the adsorption isotherm of hydrogels. Figure 6d shows the ARIAN model for the MB adsorption of P(NIPAM-co-AAc)/MoS2 at room temperature. First, several data (region I) were fit in the Henry equation (eq 5), and the rest of them (region II) were fit in the Temkin equation (eq 6). Because the adsorbent surface in our work is nonideal, it is not appropriate to use the Langmuir isotherm to fit. The Temkin equation is a suitable equation for the nonideal surface. The adsorption equilibrium constants can be obtained using them. Table 4 shows the ARIAN model isotherm parameters for the adsorption of MB onto P(NIPAM-co-AAc)/MoS2 hydrogels at room temperature. As shown in Table 4, the parameters of \( K \) and \( R^2 \) for Henry’s Law are 4.927 and 0.983, respectively. In addition, \( C_1 \), \( C_2 \), and \( R^2 \) for the Temkin equation are 247.5, 0.068, and 0.955, respectively. The maximum experimental \( q_e \) is equal to the experimental \( q_e \) of 916 mg/g (initial MB concentration of 640 mg/L) after 650 min but not values calculated by the Langmuir model. Actually, Langmuir and Freundlich isotherm parameters for the adsorption of MB onto P(NIPAM-co-AAc)/MoS2 hydrogels at room temperature were calculated and their \( R^2 \) values were 0.994 and 0.950, respectively, which is much higher than that of 0.955 obtained by the ARIAN model. It can be seen that the adsorption isotherm of the P(NIPAM-co-AAc)/MoS2 composite hydrogel for MB at room temperature is more consistent with the Langmuir adsorption isotherm model. According to the Langmuir isotherm adsorption model simulation, the maximum adsorption capacity of the P(NIPAM-co-AAc)/MoS2 composite hydrogel can reach 1258 mg/g. Actually, in most literature studies, the adsorption isotherm was well fitted with the Langmuir model. To better compare our results with the reported data in the literature, we would keep the results and discussion on the modeling of Langmuir and Freundlich isotherm.

Table 3. Langmuir and Freundlich Isotherm Parameters for the Adsorption of MB onto P(NIPAM-co-AAc)/MoS2 Hydrogels at Room Temperature

| sample                         | Langmuir isotherm parameters | Freundlich isotherm parameters |
|--------------------------------|-----------------------------|--------------------------------|
| P(NIPAM-co-AAc)/MoS2           | 1258                        | 34.7                           |
|                                | 0.0051                      | 0.523                          |
|                                | 0.994                       | 0.950                          |

Table 4. ARIAN Model Isotherm Parameters for the Adsorption of MB onto P(NIPAM-co-AAc)/MoS2 Hydrogels at Room Temperature

| sample                         | Henry’s Law | Temkin                      |
|--------------------------------|-------------|-----------------------------|
|                                | K           | R²                          |
| P(NIPAM-co-AAc)/MoS2           | 4.927       | 247.5                       |
|                                | 0.983       | 0.068                       |
|                                | 0.983       | 0.955                       |
on the wider channels interact with MB in the structure of the hydrogel, the most active sites located adsorption site on the surface of the hydrogel. Due to changes sca

Developed to treat MB dyes in sewage. Table 5 lists the molecules.

Numbers of adsorption sites of NG-4 are exposed to MB 90 to 715 mg/g for MB. Some representative work including for MB.

Advantage and shows a high adsorption capacity of 1258 mg/g. The adsorption performance of the P(NIPAM-co-Ac)/MoS2 composite hydrogel at different temperatures, it is observed that as the temperature increases to 40 °C, the adsorption performance of the P(NIPAM-co-Ac)/MoS2 composite hydrogel is weakened. The adsorption isotherm of the P(NIPAM-co-Ac)/MoS2 composite hydrogel for MB at room temperature conforms to the Langmuir isotherm adsorption model. The adsorption process of MB by the P(NIPAM-co-Ac)/MoS2 composite hydrogel at room temperature fit well the pseudo-second-order kinetics model. This research provides a facile method for developing dye adsorption materials with high adsorption capacity.

EXPERIMENTAL SECTION

Chemicals and Materials. N-Isoproylacrylamide (NIPAM, 99%), acrylic acid (AAc, 98%), and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Molybdenum disulfide (MoS2) was obtained from Jiangsu XFNANO Materials Tech Co., Ltd. (Nanjing, China). Photoinitiator 2960 (99%) was obtained from Shanghai Yinchang New Material Co., Ltd. (Shanghai, China). N,N’-Methylenebisacrylamide (MBA, 98%) was purchased from J&K Scientific Ltd. (Beijing, China). Methylene blue (MB) was purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade, and the water used in all experiments was deionized water.

Preparation of P(NIPAM-co-Ac) and P(NIPAM-co-Ac)/MoS2 Composite Hydrogels. NIPAM (1 g) and 0.1 g of AAc were weighed and dissolved in an appropriate amount of deionized water. MBA (2.72 mg) and 20 mg of photoinitiator 2960 were added to the previous solution, and the mixture was shaked until an aqueous solution was obtained. A certain amount of MoS2 required was added to the deionized water and then mixed in an ultrasonic cell pulverizer for 30 min. The MoS2 dispersion was combined with the solution containing monomers, cross-linker, and initiator and placed in an ice–water bath. The reaction was allowed to take place in a 365 nm low-pressure mercury lamp catalytic reaction device for 4 h under ultraviolet light irradiation. Changing the MoS2 mass from 0 to 25 mg, a series of P(NIPAM-co-Ac/MoS2) composite hydrogels and the P(NIPAM-co-Ac) hydrogel without MoS2 can be prepared.

Characterization of Hydrogels. Fourier Transform Infrared Spectroscopy (FT-IR). The freeze-dried P(NIPAM-co-Ac) and P(NIPAM-co-Ac)/MoS2 hydrogel samples were ground into powder in a mortar and mixed with KBr to form tablets. Then, a Fourier infrared spectrometer (Nicolet, Avatar370) was used for the test.

Raman Spectroscopy (Raman). The freeze-dried P(NIPAM-co-Ac) and P(NIPAM-co-Ac)/MoS2 hydrogel samples were ground into powder. A DXR Laser Raman

Table 5. Adsorption Isotherm Constants of Some Adsorbents for MB

| adsorbents                              | q_e (mg/g) | references |
|-----------------------------------------|------------|------------|
| β-cyclodextrin/poly(acrylic acid) grafted onto graphene oxide (β-CD/PAA/GO) hydrogels | 248        | 64         |
| polydopamine microspheres               | 90.7       | 58         |
| the modified banana pseudo-stem cellulose backbone with sodium acrylate (NaAc) and acrylamide (AM) onto (BCPCMC-g-poly(NaAc-co-AM)) | 333        | 59         |
| mesoporous carbon material from fishery waste | 184.4     | 60         |
| cellulose nanocrystal-alginate hydrogel beads | 255.5     | 65         |
| core@double-shell-structured magnetic halloysite nanotube | 714.39    | 61         |
| polyacrylamide/chitosan/Fe3O4 composite hydrogels | 1603       | 28         |
| poly(acrylic acid)/laponite hydrogel    | 3846       | 62         |
| villilike polylactic (acrylic acid)-based hydrogel | 2249      | 63         |
| P(NIPAM-co-Ac)/MoS2 hydrogels           | 1258       | this work  |

\[ q_e = KC_e \]

where K is the binding constant of the adsorbate on the surface and adsorption increases linearly with the concentration.

\[ q_e = C_1 \ln(C_2/C_0) \]

where C1 is a constant and C2 is the adsorption equilibrium constant.

At room temperature and 40 °C, there is one kind of adsorption site on the surface of the hydrogel. Due to changes in the structure of the hydrogel, the most active sites located on the wider channels interact with MB first. After sufficiently increasing the concentration of MB in the adsorbent, they interact with adsorption sites in a narrower space. MoS2 stabilizes the hydrogel structure and makes its channels or internal space wider. MoS2 acts in the adsorbent like a scaffolding for hydrogel. Thus, in spite of the fact that the amount of MoS2 in NG-4 is more than that in NG-1, more numbers of adsorption sites of NG-4 are exposed to MB molecules.

Nowadays, a large number of adsorbents have been developed to treat MB dyes in sewage. Table 5 lists the maximum adsorption capacity of some adsorbents. In Table 5, most of the work reported show the adsorption capacity from 90 to 715 mg/g for MB. Some representative work including polyacrylamide/chitosan/Fe3O4 composite hydrogels, poly-(acrylic acid)/laponite hydrogel, and villilike poly(acrylic acid)-based hydrogel has also been listed in Table 5. It can be seen that the maximum adsorption capacity of 1603, 3846, and 2249 mg/g for MB is reported, respectively. Compared with the adsorbents reported in the literature, the P(NIPAM-co-Aac)/MoS2 composite hydrogel in this work still has an advantage and shows a high adsorption capacity of 1258 mg/g for MB.

CONCLUSIONS

Through the analysis of FT-IR, Raman, and SEM, it is proved that the P(NIPAM-co-Ac)/MoS2 composite hydrogel was successfully prepared by simple free radical polymerization. SEM images of the cross section of the P(NIPAM-co-Aac)/MoS2 composite hydrogel showed that the composite hydrogel had a porous network structure. Hydrogels are hydrophilic and can absorb large amounts of water. By studying the swelling properties of P(NIPAM-co-Aac) and P(NIPAM-co-Aac)/MoS2 hydrogels, the results show that MoS2 can increase the swelling ratio of P(NIPAM-co-Aac) to a certain extent due to its negatively charged surface. The P(NIPAM-co-Aac)/MoS2 composite hydrogel with 25 mg of MoS2 can have a swelling ratio of nearly 176.50. The addition of MoS2 can effectively improve the adsorption performance of the P(NIPAM-co-Aac) hydrogel. When the initial concentration of MB is 640 mg/L, the maximum adsorption capacity calculated by the Langmuir isotherm adsorption model can reach about 1258 mg/g. By studying the adsorption performance of the P(NIPAM-co-Aac)/MoS2 composite hydrogel at different temperatures, it is observed that as the temperature increases to 40 °C, the adsorption performance of the P(NIPAM-co-Aac)/MoS2 composite hydrogel is weakened. The adsorption isotherm of the P(NIPAM-co-Aac)/MoS2 composite hydrogel for MB at room temperature conforms to the Langmuir isotherm adsorption model. The adsorption process of MB by the P(NIPAM-co-Aac)/MoS2 composite hydrogel at room temperature fit well the pseudo-second-order kinetics model. This research provides a facile method for developing dye adsorption materials with high adsorption capacity.
microscope from Thermo Fisher Scientific (United States) was employed for testing. The laser wavelength of the Raman spectrometer used was 532 nm.

Scanning Electron Microscope (SEM). The freeze-dried hydrogel sample was brittle fractured in liquid nitrogen, and then the cross section of the hydrogel was sprayed with gold. Then, the hydrogel was observed using the JEOL-6360LA scanning electron microscope (JEOL Ltd., Japan).

Transmission Electron Microscope (TEM). The ethanol dispersion of MoS2 particles was dropped onto a copper mesh, and its morphology and size were observed with a Japanese JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV.

ζ-Potential Analysis. The low-concentration MoS2 dispersion was sonicated for 30 min. The ζ-potential of MoS2 particles in aqueous solutions was measured at 25 °C with a Malvern Zetasizer Nano ZS.

Swelling Ratio. At room temperature, 10 mg of the freeze-dried P(NIPAM-co-AAc) and P(NIPAM-co-AAc)/MoS2 composite hydrogel samples were added into 50 mL of water. The sample was taken out of the water at regular intervals, and the surface water was wiped with filter paper; its mass was weighed with a precision electronic balance. Equation 7 was used to calculate the swelling ratio WSR (g/g) of the hydrogel.

\[
WSR = \frac{W_t - W_0}{W_0}
\]  

where \( W_0 \) and \( W_t \) represent the initial dried sample weight and the weight of the swollen sample at time \( t \), respectively.

Dye Adsorption Experiment. Drawing the Standard Curve. First, 100 mL of MB solution at a concentration of 640 mg/L was prepared and then diluted with deionized water to different concentrations (64, 32, 16, 6.4, 3.2, 1.6, 0.8, and 0.64 mg/L). A UV–vis spectrophotometer (UV-1800, Shimadzu Corporation, Japan) was used to measure the absorbance at a wavelength of 664 nm. A standard curve (absorbance vs MB concentration) was created. The value for the unknown sample was determined by comparing it with the standard curve.

Adsorption Process. First, 100 mL of MB solution at a concentration of 640 mg/L was prepared and diluted with deionized water to different concentrations for adsorption experiments. The freeze-dried hydrogel samples were added into a series of prepared MB solutions with different concentrations to perform dye adsorption experiments at room temperature or 40 °C. The absorbance of the solution was measured at regular intervals; its concentration was obtained from the standard curve, and the corresponding adsorption capacity was calculated according to eq 8.

\[
Q_t = \frac{V(C_0 - C_t)}{W_0}
\]  

where \( Q_t \) (mg/g), \( C_0 \) (mg/L), \( C_t \) (mg/L), \( V \) (L), and \( W_0 \) (g) represent the adsorption capacity at time \( t \), the initial MB concentration, residual MB concentration at time \( t \), the volume of MB solution, and the weight of the dried hydrogel sample. Similarly, to study the effect of the initial dye solution concentration on adsorption, the adsorption equilibrium of the MB dye on the hydrogel was studied at a concentration of 6.4–640.0 mg/L at room temperature and 40 °C.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04433.

Thermogravimetric analysis of hydrogels; coefficients of the KASRA equation; and adsorption kinetic KASRA model (PDF)

AUTHOR INFORMATION
Corresponding Authors
Jianping Yang — Department of Orthopedics, Changzhou Hospital of Traditional Chinese Medicine, Changzhou 213000 Jiangsu, P. R. China; Email: 43655304@qq.com
Zheng Cao — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164 Jiangsu, P. R. China; Changzhou University Huaide College, Jingjiang 214500, P. R. China; National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, P. R. China; Email: zcao@cczu.edu.cn, caozheng0571@hotmail.com

Authors
Kailun Wang — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164 Jiangsu, P. R. China
Zhengxiang Lv — Department of Orthopedics, Changzhou Hospital of Traditional Chinese Medicine, Changzhou 213000 Jiangsu, P. R. China
Wenjun Li — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164 Jiangsu, P. R. China
Keming Luo — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164 Jiangsu, P. R. China

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c04433

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This project was supported by the National Natural Science Foundation of China (Grant No. 21704008), Major Science and Technology Project of Changzhou Health Commission (Project No: ZD201917), Natural Science Foundation of Jiangsu Province, China (Grant No. BK20201449), and Natural Science Foundation of the Jiangsu Higher Institutions of China (Grant No. 20KJA430011). Financial support provided for this project by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), and financial support from the Young Elite Scientist Sponsorship Program of...
the Jiangsu Province Association of Science and Technology, Postgraduate Research & Practice Innovation Program of Jiangsu Province are also gratefully acknowledged.

**REFERENCES**

(1) Yakub, M. T.; Sen, T. K.; Afroz, S.; Ang, H. M. Dye and its removal from aqueous solution by adsorption: A review. Adv. Colloid Interface Sci. 2014, 209, 172–184.

(2) Kathiresan, V.; Kansedo, J.; Lau, S. Y. Efficiency of various recent wastewater dye removal methods: A review. J. Environ. Chem. Eng. 2018, 6, 4676–4697.

(3) Ahmad, A.; Mohd-Setapar, S. H.; Chuong, C. S.; Khatoon, A.; Wani, W. A.; Kumar, R.; Rafatullah, M. Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater. RSC Adv. 2015, 5, 30801–30818.

(4) Maruthapandi, M.; Kumar, V. B.; Gedanken, A. Carbon Dot Initiated Synthesis of Poly(4,4′-diaminodiphenylmethane) and Its Methylene Blue Adsorption. ACS Omega 2018, 3, 7061–7068.

(5) Cao, Z.; Gordichuk, P. I.; Loos, K.; Sudhölter, E. R.; de Smet, L. C. P. M. The effect of guanidinium functionalization on the structural properties and anion affinity of polyelectrolyte multilayers. Soft Matter 2016, 12, 1496–1505.

(6) Maruthapandi, M.; Kumar, V. B.; Luong, J. H. T.; Gedanken, A. Kinetics, Isotherm, and Thermodynamic Studies of Methylene Blue Adsorption on Poly(aniline and Polypropylene Macro–Nanoparticles Synthesized by C-Dot-Initiated Polymerization. ACS Omega 2018, 3, 7196–7203.

(7) Feng, M.; You, W.; Wu, Z.; Chen, Q.; Zhan, H. Mildly Alkaline Preparation and Methylene Blue Adsorption Capacity of Hierarchical Flower-like Sodium Titinate. ACS Appl. Mater. Interfaces 2013, 5, 12654–12662.

(8) Li, Q.; Qiao, X.-Q.; Jia, Y.; Hou, D.; Li, D.-S. Amorphous CoMoS4 Nanostructure for Photocatalytic H2 Generation, Nitrogen Reduction, and Methylene Blue Adsorption. ACS Appl. Nano Mater. 2020, 3, 68–76.

(9) Gui, C.-X.; Wang, Q.-Q.; Hao, S.-M.; Qu, J.; Huang, P.-P.; Cao, C.-Y.; Song, W.-G.; Yu, Z.-Z. Sandwich-like Magnesium Silicate/Reduced Graphene Oxide Nanocomposite for Enhanced Pb2+ and Methylene Blue Adsorption. ACS Appl. Mater. Interfaces 2014, 6, 14653–14659.

(10) Li, Y.; Fan, C.; Kamdem, P.; Jin, X.-J. Binder-Free Two-Dimensional MXene/Acid Activated Carbon for High-Performance Supercapacitors and Methylene Blue Desorption. Energy Fuels 2020, 34, 10120–10130.

(11) Ortega, P. F. R.; Trigueiro, J. P. C.; Santos, M. R.; Denadai, Â. M. L.; Oliveira, L. C. A.; Teixeira, A. P. C.; Silva, G. G.; Lavall, R. L. Thermodynamic Study of Methylene Blue Adsorption on Carbon Nanotubes Using Isothermal Titration Calorimetry: A Simple and Rigorous Approach. J. Chem. Eng. Data 2017, 62, 729–737.

(12) Ramos, J.; Imaz, A.; Forcada, J. Temperature-sensitive nanogels: poly(N-vinylcaprolactam) versus poly(N-isopropylacrylamide). Polym. Chem. 2012, 3, 852–856.

(13) Wiedemair, J.; Serpe, M. J.; Kim, J.; Masson, J.-F.; Lyon, L. A.; Mizaikoff, B.; Krantz, In-Situ AFM Studies of the Phase-Transition Behavior of Single Thermoresponsive Hydrogel Particles. Langmuir 2007, 23, 130–137.

(14) Cao, Z.; Du, B.; Chen, T.; Li, H.; Xu, J.; Fan, Z. Fabrication and Properties of Thermosensitive Organic/Inorganic Hybrid Hydrogel Thin Films. Langmuir 2008, 24, 5543–5551.

(15) Schmidt, S.; Hellweg, T.; von Klitzing, R. Packing Density Control in P(NIPAM-co-AAc) Microgel Monolayers: Effect of Surface Charge, pH, and Preparation Technique. Langmuir 2008, 24, 12595–12602.

(16) Xia, L.-W.; Ju, X.-J.; Liu, J.-J.; Xie, R.; Chu, L.-Y. Responsive hydrogels with poly(N-isopropylacrylamide-co-acrylic acid) colloidal spheres as building blocks. J. Colloid Interface Sci. 2010, 349, 106–113.

(17) Zhang, J.; Chu, L.-Y.; Li, Y.-K.; Lee, Y. M. Dual thermo- and pH-sensitive poly(N-isopropylacrylamide-co-acrylic acid) hydrogels with rapid response behaviors. Polymer 2007, 48, 1718–1728.

(18) Boztepe, C.; Künkül, A.; Yuceer, M. Application of artificial intelligence in modeling of the doxorubicin release behavior of pH and temperature responsive poly(NIPAam-co-AAc)-PEG IPN hydrogel. J. Drug Delivery Sci. Technol. 2020, 57, No. 101603.

(19) Zhang, M.; Li, Y.; Yang, Q.; Huang, L.; Chen, L.; Ni, Y.; Xiao, H. Temperature and pH responsive cellulose filament/poly (NIPAM-co-AAc) hybrids as novel adsorbent towards Pb(II) removal. Carbohydr. Polym. 2018, 195, 495–504.

(20) Cao, Z.; Chen, T.-y.; Guo, X.-i.; Zhou, X.-j.; Nie, J.-j.; Xu, J.-t.; Fan, Z.-q.; Du, B.-y. Synthesis and properties of organic-inorganic hybrid P(NIPAM-co-AM-TMSPMA) microgels. Chin. J. Polym. Sci. 2011, 29, 439–449.

(21) Kureha, T.; Shibamoto, T.; Matsui, S.; Sato, T.; Suzuki, D. Investigation of Changes in the Microscopic Structure of Anionic Poly(N-isopropylacrylamide-co-Acrylic acid) Microgels in the Presence of Cationic Organic Dyes toward Precisely Controlled Uptake/Release of Low-Molecular-Weight Chemical Compound. Langmuir 2016, 32, 4575–4585.

(22) Naseem, K.; Begum, R.; Wu, W.; Usman, M.; Irfan, A.; Al-Sehemi, A. G.; Farooqi, Z. H. Adsorptive removal of heavy metal ions using polystyrene-poly(N-isopropylmethacrylamide-acrylic acid) core/shell gel particles: Adsorption isotherms and kinetic study. J. Mol. Liq. 2019, 277, 522–531.

(23) Cao, Z.; Guo, J.; Fan, X.; Xu, J.; Fan, Z.; Du, B. Detection of heavy metal ions in aqueous solution by P(MBTVCB-co-VIM)-coated QCM sensor. Sens. Actuators, B 2011, 157, 34–41.

(24) Jiang, C.; Ma, X.; Xue, M.; Lian, H.-z. Application of thermoresponsive hydrogel/gold nanorods composites in the detection of diquat. Talanta 2017, 174, 192–197.

(25) Parasuraman, D.; Serpe, M. J. Poly (N-Isopropylacrylamide) Microgels for Organic Dye Removal from Water. ACS Appl. Mater. Interfaces 2011, 3, 2732–2737.

(26) Wang, L.; Geng, J.; Bai, B. Highly Deformable Nano-Cross-Linker-Bridged Nanocomposite Hydrogels for Water Management of Oil Recovery. Energy Fuels 2013, 28, 3068–3076.

(27) Cao, Z.; Chen, Y.; Zhang, C.; Cheng, J.; Wu, D.; Ma, W.; Liu, C.; Fu, Z. Preparation of near-infrared laser responsive hydrogels with enhanced laser marking performance. Soft Matter 2019, 15, 2950–2959.

(28) Zhang, C.; Dai, Y.; Wu, Y.; Lu, G.; Cao, Z.; Cheng, J.; Wang, K.; Yang, H.; Xia, Y.; Wen, X.; Ma, W.; Liu, C.; Wang, Z. Facile preparation of polycrylamide/chitosan/Fe3O4 composite hydrogels for effective removal of methylene blue from aqueous solution. Carbohydr. Polym. 2020, 234, 115882.

(29) Na, Y.-H.; Kurokawa, T.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Okabe, S.; Karino, T.; Shibayama, M. Structural Characteristics of Double Network Gels with Extremely High Mechanical Strength. Macromolecules 2004, 37, 5370–5374.

(30) Cao, Z.; Zhang, Y.; Luo, K.; Wu, Y.; Gao, H.; Cheng, J.; Liu, C.; Tao, G.; Guan, Q.; Zhang, L. Preparation and Properties of Polycrylamide/Sodium Alginate Hydrogel and the Effect of Fe Adsorption on Its Mechanical Performance. J. Renewable Mater. 2021, 9, 1447–1462.

(31) Cao, Z.; Chen, Y.; Li, D.; Cheng, J.; Liu, C. Fabrication of Phosphate-Imprinted PNIPAM/SiO2 Hybrid Particles and Their Phosphate Binding Property. Polymers 2019, 11, No. 253.

(32) Liu, G.; Chunlin, L.; Yuyuan, C.; Shuai, Q.; Suyuan, Y.; Dun, W.; Haitao, X.; Zheng, C. Formation of the Self-assembled Multilayers Containing the Temperature/pH Dual-responsive Microgels. Nanosci. Nanotechnol. 2019, 9, 267–277.

(33) Cao, Z.; Hu, Y.; Yu, Q.; Lu, Y.; Wu, D.; Zhou, A.; Ma, W.; Xia, Y.; Liu, C.; Loos, K. Facile Fabrication, Structures, and Properties of Laser-Marked Polycrylamide/Bi2O3 Hydrogels. Adv. Eng. Mater. 2017, 19, No. 1600826.
(34) Cao, Z.; Chen, Y.; Zhang, Q.; Xia, Y.; Liu, G.; Wu, D.; Ma, W.; Cheng, J.; Liu, C. Preparation and ion sensing property of the self-assembled microgels by QCM. Nanofabrication 2017, 3, 16–25.
(35) Cao, Z.; Du, B.; Chen, T.; Nie, J.; Xu, J.; Fan, Z. Preparation and Properties of Thermo-sensitive Organic/Inorganic Hybrid Langmuir Microgels. 2008, 24, 12771–12778.
(36) Tang, L.; Wang, J.-j.; Wang, L.; Jia, C.-t.; Lv, G.-x.; Liu, N.; Wu, M.-h. Facile Synthesis of Silver Bromide-Based Nanomaterials and Their Efficient and Rapid Selective Adsorption Mechanisms Toward Anionic Dyes. ACS Sustainable Chem. Eng. 2016, 4, 4617–4625.
(37) Guan, Y.-F.; Marcos-Hernández, M.; Lu, X.; Cheng, W.; Yu, H.-Q.; Elimelech, M.; Villagrán, D. Silica Removal Using Magnetic Iron-Aluminum Hybrid Nanomaterials: Measurements, Adsorption Mechanisms, and Implications for Silica Scaling in Reverse Osmosis. Environ. Sci. Technol. 2019, 53, 13302–13311.
(38) Yu, Y.; Shi, Y.; Zhang, B. Synergetic Transformation of Solid Inorganic–Organic Hybrids into Advanced Nanomaterials for Catalytic Water Splitting. Acc. Chem. Res. 2018, 51, 1711–1721.
(39) Nanula, A.; Bao, C. P. Hydrogel of the Supramolecular Complex of Graphene Oxide and Sulfonatocalix[4]arene as Reusable Material for the Degradation of Organic Dyes: Demonstration of Adsorption and Degradation by Spectroscopy and Microscopy. ACS Omega 2019, 4, 5731–5740.
(40) Mozahida, M.; Lee, D. S. Photocatalytic degradation of methylene blue with P25/graphene/polyacrylamide hydrogels: Optimization using response surface methodology. J. Hazard. Mater. 2020, 400, No. 123314.
(41) Jv, X.; Zhao, X.; Ge, H.; Sun, J.; Li, H.; Wang, Q.; Lu, H. Fabrication of a Magnetic Poly(aspartic acid)-Poly(acrylic acid) Hydrogel: Application for the Adsorptive Removal of Organic Dyes from Aqueous Solution. J. Chem. Eng. Data 2019, 64, 1228–1236.
(42) Singh, N.; Rajayuddin, S.; Ghosh, K.; Mehta, S. K.; Dan, A. Chitosan-Graphene Oxide Hydrogels with Embedded Magnetic Iron Oxide Nanoparticles for Dye Removal. ACS Appl. Nano Mater. 2019, 2, 7379–7392.
(43) Basu, H.; Singh, S.; Venkatesh, M.; Pimple, M. V.; Singhahl, R. K. Graphene oxide–MoO2-goethite microsphere impregnated alginate: A novel hybrid nanosorbent for As (III) and As (V) removal from groundwater. J. Water Process Eng. 2021, 42, No. 101219.
(44) Wang, X.-l.; Qin, W.; Wang, L.-x.; Zhao, K.-y.; Wang, H.-c.; Liu, H.-y.; Wei, J.-f. Desalination of dye utilizing carbonized titanium dioxide/calcium alginate hydrogel nanofiltration membrane with high salt separation. Perm. Surf. Technol. 2020, 253, No. 117475.
(45) Zhou, J.; Hao, B.; Wang, L.; Ma, J.; Cheng, W. Preparation and characterization of nano-TiO2/chitosan/poly(N-isopropylacrylamide) composite hydrogel and its application for removal of ionic dyes. Sep. Purif. Technol. 2017, 176, 193–199.
(46) Jiang, H.; Carter, N. M.; Zareei, A.; Nejati, S.; Waimin, J. F.; Chittiboyina, S.; Niedert, E. E.; Soleimani, T.; Lelièvre, S. A.; Goergen, C. J.; Rahimi, R. A Wireless Implantable Strain Sensing Scheme Using Ultrasound Imaging of Highly Stretchable Zinc Oxide/Poly Dimethylacrylamide NanoComposite Hydrogel. ACS Appl. Bio Mater. 2020, 3, 4012–4024.
(47) Zhao, Y.; Zhang, Y.; Liu, A.; Wei, Z.; Liu, S. Construction of Three-Dimensional Hemin-Functionalized Graphene Hydrogel with High Mechanical Stability and Adsorption Capacity for Enhancing Photodegradation of Methylene Blue. ACS Appl. Mater. Interfaces 2017, 9, 4006–4014.
(48) Gopalakrishnan, D.; Damien, D.; Shaijumon, M. M. MoS2 Quantum Dot-Interspersed Exfoliated MoS2 Nanosheets. ACS Nano 2014, 8, 5297–5303.
(49) Park, H.; Liu, N.; Kim, B. H.; Kwon, S. H.; Baek, S.; Kim, S.; Lee, H.-K.; Yoon, Y. J.; Kim, S. Exceptionally Uniform and Scalable Multilayer MoS2 Phototransistor Array Based on Large-Scale MoS2 Grown by RF Sputtering, Electron Beam Irradiation, and Sulfurization. ACS Appl. Mater. Interfaces 2020, 12, 20645–20652.
(50) Kwač, J. Y.; Hwang, J.; Caldeiron, B.; Alsalman, H.; Munoz, N.; Schutter, B.; Spencer, M. G. Electrical Characteristics of Multilayer MoS2 FET’s with MoS2/Graphene Heterojunction Contacts. Nano Lett. 2014, 14, 4511–4516.
(51) Cao, Z.; Lu, G.; Gao, H.; Xue, Z.; Luo, K.; Wang, K.; Cheng, J.; Guan, Q.; Liu, C.; Luo, M. Preparation and Laser Marking Properties of Poly(propylene)/Molybdenum Sulfide Composite Materials. ACS Omega 2021, 6, 9129–9140.
(52) Schneider, R.; Facure, M. H. M.; Alvarenga, A. D.; Chagas, P. A. M.; dos Santos, D. M.; Correa, D. S. Dye Adsorption Capacity of MoS2 Nanoflakes Immobilized on Poly(lactic acid) Fibrous Membranes. ACS Appl. Nano Mater. 2021, 4, 4881–4894.
(53) Tian, C.; Xiang, X.; Wu, J.; Li, B.; Cai, C.; Khan, B.; Chen, H.; Yuan, Y.; Za, X. Facile Synthesis of MoS2/CuS Nanosheet Composites as an Efficient and Ultrafast Adsorbent for Water-Soluble Dyes. J. Chem. Eng. Data 2018, 63, 3966–3974.
(54) Chiu, D.-J.; Li, Y.; Feng, C.-K.; Yang, M.-R.; Chen, K.-S.; Swieszkowski, W. Preparation and enhanced mechanical properties of hydroxypapatite hybrid hydrogels via novel photocatalytic polymerization. J. Polym. Res. 2017, 24, No. 227.
(55) Tanabe, T.; Osaki, M.; Miyajima, M.; Kitamura, K.; Oyama, Y. Raman and TEM characterization of 2D layered MoS2 crystals grown on non-metal surfaces by friction-induced synthesis. Appl. Surf. Sci. 2021, 561, No. 150016.
(56) Hou, N.; Wang, R.; Wang, F.; Bai, J.; Zhou, J.; Zhang, L.; Hu, J.; Liu, S.; Jiao, T. Fabrication of Hydrogels via Host-Guest Polymers as Highly Efficient Organic Dye Adsorbsents for Wastewater Treatment. ACS Omega 2020, 5, 5470–5479.
(57) Rafi, M.; Samiey, B.; Cheng, C.-H. Study of Adsorption Mechanism of Congo Red on Graphene Oxide/PAMAM Nanocomposite. Materials. 2018, 11, No. 496.
(58) Fu, J.; Chen, Z.; Wang, M.; Liu, S.; Zhang, J.; Zhang, J.; Han, R.; Xu, Q. Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): Kinetics, isotherm, thermodynamics and mechanism analysis. Chem. Eng. J. 2015, 259, 53–61.
(59) Bello, K.; Sarojini, B. K.; Narayana, B.; Rao, A.; Bryappa, K. A study on adsorption behavior of newly synthesized banana pseudostem derived superabsorbent hydrogels for cathion and anionic dye removal from effluents. Carbohydr. Polym. 2018, 181, 605–615.
(60) Marrackchi, F.; Auta, M.; Khanday, W. A.; Hameed, B. H. High-surface-area and nitrogen-rich mesoporous carbon material from fishery waste for effective adsorption of methylene blue. Powder Technol. 2017, 321, 428–434.
(61) Wan, X.; Zhan, Y.; Long, Z.; Zeng, G.; He, Y. Core@double-shell structured magnetic haloysite nanotube nano-hybrid as efficient recyclable adsorbent for methylene blue removal. Chem. Eng. J. 2017, 330, 491–504.
(62) Gao, B.; Yu, H.; Wen, J.; Zeng, H.; Liang, T.; Zuo, F.; Cheng, C. Super-adsorbent poly(acrylic acid)/laponite hydrogel with ultra-high mechanical property for adsorption of methylene blue. J. Environ. Chem. Eng. 2021, 9, No. 106346.
(63) Tang, Z.; Hu, X.; Ding, H.; Li, Z.; Liang, R.; Sun, G. Villi-like poly(acrylic acid) based hydrogel adsorbent with fast and highly efficient methylene blue removing ability. J. Colloid Interface Sci. 2021, 594, 54–63.
(64) Liu, J.; Liu, G.; Liu, W. Preparation of water-soluble β-cyclodextrin/poly(acrylic acid)/graphene oxide nanocomposites as new adsorbents to remove cationic dyes from aqueous solutions. Chem. Eng. J. 2014, 257, 299–308.
(65) Mohammed, N.; Grishkewich, N.; Waeijen, H. A.; Berry, R. M.; Tam, K. C. Continuous flow adsorption of methylene blue by cellulose nanocrystal-alginate hydrogel beads in fixed bed columns. Carbohydr. Polym. 2016, 136, 1194–1202.