Controllable synthesis and adsorption mechanism of flower-like MoS2/g-C3N4 nanocomposites for removal of methylene blue in water

Zhentao Wang  
Northwestern Polytechnical University

Jaafar Hasan  
Northwestern Polytechnical University

Jingjing Wang  
Northwestern Polytechnical University

Caiwei Zhang  
Northwestern Polytechnical University

Waheed Iqbal  
Northwestern Polytechnical University

Ninghui Chang  
Northwestern Polytechnical University

Chuanguang Qin (✉ qinchg@nwpu.edu.cn)  
Northwestern Polytechnical University  https://orcid.org/0000-0003-4849-0187

Research Article

Keywords: Flower-like MoS2/g-C3N4, Adsorption, Methylene blue (MB), Mechanism, Ecological assessment

Posted Date: October 7th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-924254/v1

License: ☑️ This work is licensed under a Creative Commons Attribution 4.0 International License.  
Read Full License
Abstract

The fabrication and adsorption mechanism of flower-like MoS$_2$/g-C$_3$N$_4$ nanocomposites as new adsorbent materials were investigated by batch sorption experiments in this paper. The influence of factors such as pH, adsorbent dosage, concentration and temperature on the adsorption properties of flower-like MoS$_2$/g-C$_3$N$_4$ nanocomposites were studied in detail. The adsorption isotherm data was fitted with the Langmuir model, and the adsorption kinetic characteristics conform to the quasi second-order kinetic equation. Thermodynamic data showed that the adsorption process of methylene blue (MB) was feasible, endothermic and spontaneous. At 45 ℃, the maximum adsorption capacity was 278.4 mg/g. The adsorbed MB solution was used to water the wheat and chickpea plants within 15 days. Compared with MB solution, the treated MB solution made the plants grow much more better.

1. Introduction

With remarkable industrial development and the continuous growth of the global population, people's demand for textile and clothing is increasing, which resulted in the continuous discharge of distinctive toxic pollutants into the water streams that raises serious environmental problems (Pan et al., 2016). Considering that in the textile, leather and paper industries, about 80% of the dye wastewater is discharged into the water without any treatment every year, which has brought very serious damage to the water supply environment, and has become a major problem that seriously threatens the quality of the biosphere and drinking water supply around the world (Carolin et al., 2017; Katheresan et al., 2018; Oladipo & Gazi, 2014).

Dye wastewater mainly comes from the production industry of dyes and dye intermediates, which is composed of mother liquor of various products and intermediates crystallization, materials lost in the production process and sewage washing the ground, among which organic dye wastewater accounts for a large proportion. Most organic dyes have certain biological toxicity, which can threaten the health of organisms in the water and even cause their death. At present, the commonly used methods for the treatment of printing and dyeing wastewater include photocatalytic degradation (Pang et al., 2018), adsorption (Yu et al., 2018), biological treatment (Wang et al., 2013), filtration (Zanacic et al., 2016) and membrane technology (Farhat et al., 2016). Because the adsorption method is low cost, effective, easy to operate and not easy to cause secondary pollution, it has gradually become an indispensable solution for printing and dyeing wastewater treatment (Gao et al., 2016; Wang et al., 2019). The effect of dye wastewater treatment by adsorption method mainly depends on the adsorbent structure and surface morphology, so the preparation of adsorbent with good adsorption performance is the key to achieve efficient treatment of dye wastewater.

There has been extensive research on the preparation and modification of adsorption materials, among which carbon materials is the most representative. It has a large specific surface area and good adsorption performance, and is the most widely used adsorbent (L. Chen et al., 2017; Manilo et al., 2016; Murray & Ormeci, 2018). More and more attention has been paid to obtaining cheap and easily available
materials with large specific surface area, unique structural properties and excellent chemical stability. Graphite phase carbon nitride is a new type of non-metallic graphite semiconductor material, which has the advantages of good stability, metal-free “earth abundant nature” and many adsorption sites (Wu et al., 2018). It showed excellent application prospects in the field of adsorption (Hu et al., 2015; Zhang et al., 2016). However, the bulk g-C$_3$N$_4$ synthesized directly from organic precursors often has a smaller specific surface area (less than 20 m$^2$·g$^{-1}$), and meagre mass/diffusion transfer rate. From a practical perspective, particularly in adsorption, the establishment of controlled porosity and morphology at the nanoscale in bulk g-C$_3$N$_4$ is essential to maximize its efficiency. In 2013, Galen D. Stucky and co-workers synthesized carbon nitride mesoporous hollow spheres by changing the precursor materials, which greatly improved the specific surface area and adsorption sites (Jun et al., 2013). MoS$_2$, indicating that a large number of sulfides (S$^{2-}$) can absorb various heavy metal and organic pollutants through electrostatic, hydrophobic or chemical complex interactions (Li et al., 2018; Liu et al., 2019). Ibrahim M. Alarifi and his colleagues synthesized and used MoS$_2$ adsorption to adsorb Congo red, at 50°C, the maximum adsorption capacity was 80.64 mg/g (Alarifi et al., 2021). Therefore, we assembled MoS$_2$ onto g-C$_3$N$_4$ to prepare MoS$_2$/g-C$_3$N$_4$ nanocomposites which can combine their excellent properties.

As a common organic dye, methylene blue (MB) is widely used in production, life and scientific research. Studying the adsorption of adsorbent on MB waste liquid can provide an economic and effective method for water pollution treatment. In order to obtain a new adsorbent with good adsorption effect on methylene blue, we synthesized flower-like MoS$_2$/g-C$_3$N$_4$ nanocomposites via hydrothermal reaction (Scheme 1). According to the experimental results, the flower-like MoS$_2$/g-C$_3$N$_4$ nanocomposites have obvious adsorption for MB. Especially at 45 °C, the maximum adsorption capacity of the flower-like MoS$_2$/g-C$_3$N$_4$ nanocomposites is 278.4 mg/g. This adsorption capacity is better than many adsorbents reported previously. In addition, the adsorption of MB on the nanocomposites has good recyclablility, and it still has good stability after five cycles. We studied the factors affecting MB adsorption (pH, adsorbent dose and original MB concentration), the adsorption isotherm model, adsorption kinetics and thermodynamics. Additionally, we introduced the applicability of the report study of the treated solution. The effluent from the MB removal process is then used to water wheat and chickpeas to examine their effects on plant growth.

### 2. Experimental Section

#### 2.1 Materials

Melamine, cyanuric acid and Na$_2$MoO$_4$·2H$_2$O were from Aladdin Chemical Reagent Co., Ltd (Shanghai, China), dimethyl sulfoxide and thiourea were from Guangdong Guanghua Sci-Tech Co., Ltd (Guangdong, China). All chemical substances were analytically pure.

#### 2.2 Preparation of g-C$_3$N$_4$ hollow sphere
The nanocomposite was synthesized on the basis of Refs (Jun et al., 2013; S. Zhao et al., 2020). First, added 1 g melamine to 50 ml dimethyl sulfoxide (DMSO), added 1 g cyanuric acid to 25 ml DMSO, stirred for 30 minutes to form a solution, and labeled as A and B. Then, in the process of stirring, dropped solution B into solution A and continued stirring for 30 minutes to form white precipitate. After the reaction, the supernatant was discarded, the precipitate washed and centrifuged, dried at 50 °C for 6 h, and ground into powder, named as MCA. Finally, the MCA was heated to 550 °C for 3 h in muffle furnace to obtain spherical g-C₃N₄.

2.3 Preparation of MoS₂/g-C₃N₄ nanocomposites

First, 0.29 g of Na₂MoO₄·2H₂O was added in 40 ml water, and form a solution. Subsequently, 0.005 g of polyvinyl pyrrolidone (PVP) was added in the solution and magnetically stirred for 10 min. After that, hydrochloric acid was added to adjust the solution pH to 1. Then, 1.44 g of thiourea was added, and ultrasonic dispersion was carried out for 10 min to form a solution. 0.192 g g-C₃N₄ was put into the solution, and ultrasonic oscillation was carried out for 2 h. Finally, the reaction mixture was transferred to a high-temperature reactor, and reacted at 220 °C for 18 h. After the reaction, the product was washed, centrifuged and dried at 50 °C for 6 h to obtain MoS₂/g-C₃N₄. Pure MoS₂ can be obtained without adding g-C₃N₄.

2.4 The study of plant growth.

First, 10 seeds of wheat and chickpea of the same shape and size were selected and sprouted in wet cotton day and night. And then planted the seeds in the same amount on the test tube with the same amount of MB solution (40 mg/L) and the treated solution (MB solution adsorbed by MoS₂/g-C₃N₄ nanocomposites). After that, these plants' root and bud growth was analyzed in the next 15 days (Gunture, Aggarwal, et al., 2020; Gunture, Kaushik, et al., 2020; Gunture et al., 2019).

2.5 Characterization of materials

The prepared adsorbents were characterized by XRD (Bruker D2 PHASER X) using Cu kα as the irradiation source (λ = 1.5418 Å). The chemical composition and electronic state of the adsorbents were studied by XPS (Kratos Axis Ultra DLD). The adsorbents’ appearance was recorded by FESEM (FEI Verios G4). And the structural details of the adsorbents were confirmed by HRTEM (FEI Talos F200X TEM). BET (3H-2000PS2) of Beishide Instrument Technology Co., Ltd. (Beijing, China) was used to carry out a nitrogen adsorption-desorption experiment on the adsorbent. The UV-Vis spectrophotometer made by Shanghai Jinhua Instrument was used to analyze the absorbance of the solution.

2.6 Adsorption procedure

Different mass of MoS₂/g-C₃N₄ nanocomposites were added into 50 ml MB solution. The different original concentrations were C₀ (mg/L). After that, the solution in the round bottom flask was heated at different temperatures (15°C, 25°C, 35°C, 45°C) with stirring at 300 rpm for about 60 minutes (until adsorption equilibrium was reached). Adjust the solution pH to 1–11 by HCl or NaOH. After adsorption,
centrifugation, take the supernatant. Then, the absorbance of MB at the maximum absorption wavelength (664 nm) was measured by UV spectrophotometer, and after the adsorption equilibrium, the equilibrium concentrations were $C_e$ (mg/L), the removal efficiency ($\eta\%$) and equilibrium adsorption capacity ($q_e$) of MB solution were counted by these formula:

$$\eta(\%) = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}$$

where $V$ (L) was the volume of MB solution, $m$ (g) was the weight of MoS$_2$/g-C$_3$N$_4$ nanocomposites and $q_e$ (mg/g) was the adsorption capacity at equilibrium.

3. Results And Discussion

3.1 Structure characterization

The powder XRD patterns of the g-C$_3$N$_4$, MoS$_2$ and MoS$_2$/g-C$_3$N$_4$ nanocomposites were shown in Fig. 1. In the typical XRD pattern, all diffraction peaks of g-C$_3$N$_4$ correspond to the standard card (JCPDS 87-1526). At 13.2 °, the peak value corresponds to the (100) crystal planes, caused by the periodic arrangement of stacking units between layers of g-C$_3$N$_4$. The peak value at 27.5 ° corresponds to the (002) crystal planes, which is the characteristic peak of the accumulation of graphite like layered structure of g-C$_3$N$_4$ (Lin et al., 2019). The diffraction peaks of pure MoS$_2$ at 15.1 °, 32.7 °, 35.2 °, 38.8 °, 44.2 ° and 57.3 ° belongs to the (002), (100), (102), (103), (006) and (110) crystal planes of hexagonal MoS$_2$ (JCPDS 37-1492), respectively (Ali et al., 2019). From this typical XRD patterns of MoS$_2$/g-C$_3$N$_4$ nanocomposites, we can see the peak of MoS$_2$ clearly, but the peak value of g-C$_3$N$_4$ is very small, which may be due to the nanocomposites contain the relatively low content of g-C$_3$N$_4$. The other possible reason of weak intensity of (002) peak of g-C$_3$N$_4$ may coincides or interfere with the (100) crystal planes of MoS$_2$ peak. Nevertheless, the diffraction peak intensity of MoS$_2$ decreases with the addition of g-C$_3$N$_4$, especially at 15.1 ° peak. This indicates that the addition of g-C$_3$N$_4$ further limits the accumulation of the molybdenum disulfide layer (Y. X. Chen et al., 2017).

XPS analysis further determined the chemical state and element composition of the MoS$_2$/g-C$_3$N$_4$ nanocomposites. Figure 2a illustrated the XPS survey spectrum confirmed C, N, Mo, and S elements exist in MoS$_2$/g-C$_3$N$_4$ nanocomposites. Figure 2b represents the spectra of C1s, where 284.1 eV corresponds to the C-C in aromatic rings, 285.8 eV corresponds to N-C = N and 288.0 eV corresponds to C-NH$_2$ (Yi et al.,}
Figure 2c suggests that the peaks of N 1s spectra at 398.6 eV, 399.1 eV and 403.8 eV belong to C = N-C, N-(C)₃ and N–H structures, respectively (Cao et al., 2017). In addition, the two peaks in the Mo 3d spectrum at around 228.95 eV and 232.13 eV belong to Mo 3d⁵/₂ and Mo 3d³/₂ in Fig. 2d, respectively. There was another peak of 226.01 eV in this area which is part of S 2s. The spectrum of S 2p in Fig. 2e shows two peaks: 161.87 eV and 163.20 eV were due to s 2p₃/₂ and s 2p₁/₂, respectively. These studies confirmed the successful preparation of MoS₂/g-C₃N₄ nanocomposites.

The morphology and structures of pure g-C₃N₄, pure MoS₂ and MoS₂/g-C₃N₄ nanocomposites were directly analyzed by SEM and TEM. Figure 3 (a-b) FESEM analysis confirmed that the as prepared g-C₃N₄ possessed the hollow sphere morphology, and Fig. 3a shows that the precursor MCA of g-C₃N₄ is spherical-like. Figure 3b shows the g-C₃N₄ formed after calcination of MCA, which is hollow and spherical. Figure 3c shows pure MoS₂, which is flower-like. Figure 3d indicates that the morphology of the MoS₂/g-C₃N₄ nanocomposites basically keeps the appearance of MoS₂. Figure 3e shows the HRTEM micrograph of MoS₂/g-C₃N₄ nanocomposites. The figure shows that MoS₂ is flower like structure, and g-C₃N₄ is coated by MoS₂. Figure 3f shows the presence of well-defined lattice fringes of 0.62 nm, this can be attributed to the (002) crystal plane of MoS₂ (Monga et al., 2020).

Figure S1 showed the N₂ adsorption desorption isotherm. Since there was almost no adsorption limitation at the high-pressure stage, the adsorption isotherm of MoS₂/g-C₃N₄ nanocomposites was determined to be type-IV isotherm with H3 type hysteresis loops, were closely related to the capillary condensation phenomenon of slit pores generated by the stacking of lamellar particles (Liu et al., 2020; Zhu et al., 2020). The pore size of MoS₂/g-C₃N₄ nanocomposites was mainly between 2–17 nm, this indicates the composite was mesoporous. It can be seen in Table S1, the BET surface area, average pore size and pore volume of MoS₂/g-C₃N₄ nanocomposites were 70.656 m²/g, 15.4494 nm and 0.2729 cm³/g, respectively. These sufficient parameters indicated that mesoporous MoS₂/g-C₃N₄ nanocomposites have excellent adsorption properties for MB.

### 3.2 Experiment majorization

#### 3.2.1 Effect of pH value

The pH value has great influence on the ionization degree of MB molecule and the surface charge of adsorbent in the solution (I et al., 2020). For the sake of studying the effect of pH value on MB adsorption, we set the pH value from 1 to 11. In Fig. S2, the MB adsorption efficiency of MoS₂/g-C₃N₄ nanocomposites increased with the pH value in the range of 1 to 11. And the surface charge of MoS₂/g-C₃N₄ nanocomposites was shown in Fig. S3. At relatively low pH, the proton ions in the solution may compete with the active sites of cationic dye MB and MoS₂/g-C₃N₄ nanocomposites, which inhibits the adsorption of MB on synthetic adsorbent. With the increase of pH, the surface charge of MoS₂/g-C₃N₄ nanocomposites became lower, resulting in stronger electrostatic attraction between MB and adsorbents. The results showed that the higher the pH value was, the higher the adsorption efficiency was. Fig. S4
showed that the MoS$_2$/g-C$_3$N$_4$ nanocomposites have higher adsorption efficiency when pH = 7, compared with g-C$_3$N$_4$ and MoS$_2$.

### 3.2.2 Effect of adsorbent dosage

By adding different amounts of MoS$_2$/g-C$_3$N$_4$ nanocomposites into MB solution, the effects of adsorption dose on adsorption efficiency and adsorption capacity were tested. *Fig. S5* illustrated when the adsorbent dosage increases, the adsorption efficiency of MB first increases, and then almost remains unchanged, the equilibrium adsorption capacity of MB decreased from 251.2mg/g to 99.7mg/g. This was due to the equilibrium state of the adsorption process, the adsorbent can no longer adsorb MB. It is obvious that a high MB adsorption rate can be achieved even with a small amount of adsorbent. Considering the removal efficiency and practicability, we selected 10mg adsorbent for the following experiments.

#### 3.2.3 Effect of MB concentration

The adsorption capacity and adsorption efficiency of the nanocomposites were tested by adding different concentrations of MB solution. *Fig. S6* showed that when MB concentration increased from 20mg/L to 100mg/L, the equilibrium adsorption capacity increased from 98.8mg/g to 227.4mg/g. It may be that with the increase of MB concentration, the adsorbate in solution has stronger driving force to overcome the mass transfer resistance between solution and adsorbent (L. Zhao et al., 2020). But with the increase of MB concentration, the adsorption rate of MB reduced from 98.80–45.48%, because at a certain concentration, the active center of the adsorbent reached saturation.

#### 3.2.4 Effect of adsorption temperature

In this work, the temperatures were set at 15 °C, 25 °C, 35 °C and 45 °C, respectively. *Fig. S7* showed that temperature had obvious influence on MB adsorption. With the increase of temperature from 15 °C to 45 °C, the adsorption efficiency rose from 86.84–98.17%. Because when the temperature increased, the molecular Brownian motion will accelerate, and low temperature will usually reduce the diffusion rate of MB in the nanocomposites (Fu et al., 2017). Considering the adsorption efficiency and practicability, the following experiments were carried out at 25 °C.

#### 3.2.5 Recyclability of MoS$_2$/g-C$_3$N$_4$ for the MB adsorption

The recyclability and stability of adsorbents can greatly improve efficiency and reduce cost. In this study, MB was desorbed with 0.1mol/L NaOH. *Fig. S8* showed the MB adsorption efficiency of MoS$_2$/g-C$_3$N$_4$ nanocomposites for five consecutive cycles. The results illustrated that the adsorption efficiency of MB decreased gradually because the adsorbate could not be completely desorbed and occupied some active adsorption sites. The adsorption efficiency of the MoS$_2$/g-C$_3$N$_4$ nanocomposite for MB was still 73.58% after five cycles, which showed that the adsorbent has good reusability.

### 3.3 Adsorption kinetics
Figure 4a showed the effect of contact time on adsorption capacity. With the increase of contact time, the adsorption capacity increased rapidly from the beginning to slowly until the adsorption equilibrium reached 60 minutes. In this study, pseudo-first-order, pseudo-second-order kinetics and intra-particle diffusion models were used to analyze the adsorption process (Tehrani & Zare-Dorabei, 2016). The calculation formula of the pseudo-first-order kinetics model was as follows:

$$\ln(q_e - q_t) = \ln q_e - tk_1$$  \hspace{1cm} (3)

The calculation formula of pseudo-second-order model was as follows:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (4)

The calculation formula of intra-particle diffusion model was as follows:

$$q_t = k_3t^{0.5} + C$$  \hspace{1cm} (5)

Where $q_e$ (mg/g) is described above, $q_t$ (mg/g) represent the adsorption capacity at any contact time, and $t$ (min) is the adsorption time. $k_1$, $k_2$ and $k_3$ are the pseudo-first-order, pseudo-second-order and intra-particle diffusion model rate constants respectively. $C$ (mg/g) is the intercept obtained by fitting the model of intra-particle diffusion.

The linear fitting results of the two kinetic models were shown in Fig. 4. It illustrated that the pseudo-second-order model (Fig. 4c) is better than the pseudo-first-order model (Fig. 4b) in describing the process of adsorption kinetics, which is proved by the higher $R^2$ ($R^2 = 0.9999$) value. In addition, the calculated results of the two kinetic models were shown in the Table S2. Theoretical equilibrium adsorption capacity $q_e$ (cal) of the pseudo-second-order model is more consistent with the experimental data $q_e$ (exp), which indicates that the adsorption of MB on MoS$_2$/g-C$_3$N$_4$ nanocomposites conforms to the pseudo-second-order model, and the adsorption process is mainly controlled by chemical adsorption (Fang et al., 2018; Guan et al., 2017).

The model of intra-particle diffusion after fitting is shown in (Fig. 4d). The graph was nonlinear, which proved that intra-particle diffusion was not the only factor limiting particle diffusion. There are three processes for MB adsorption. The first stage was from the solution to the surface of MoS$_2$/g-C$_3$N$_4$ nanocomposites. The second stage was the diffusion of MB in MoS$_2$/g-C$_3$N$_4$ nanocomposites. The third stage was the final balance stage. The above analysis showed that the intra-particle diffusion and surface adsorption occur simultaneously, which affects the adsorption of MB significantly.

### 3.4 Adsorption isotherm
Figure S9 showed the MB adsorption isotherms of MoS$_2$/g-C$_3$N$_4$ nanocomposite at different temperatures. The experimental data were fitted into Langmuir model for monolayer adsorption (Eq. (6)) and Friedrich model of multilayer adsorption (Eq. (7)) (Gunture, Kaushik, et al., 2020). They can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$$

where $C_e$ (mg/L) was the equilibrium concentration of MB, $q_m$ (mg/g) was the theoretical maximum adsorption capacity, $K_L$ (L/mg) and $K_F$ were Langmuir constant and Friedrich constant, respectively. $n$ was the constant related to the surface inhomogeneity of adsorbent (L. Zhao et al., 2020).

The fitting results of the two isotherm models were shown in Fig. 5. The datas in Table 1 showed that $R^2$ values in the Langmuir model (Fig. 5a) were bigger than those in the Friedrich model (Fig. 5b). Therefore, the adsorption of MB on MoS$_2$/g-C$_3$N$_4$ nanocomposites followed the Langmuir isotherm model. At 45 $^\circ$C, $q_{\text{max}}$ is 278.4 mg/g, which indicates that MoS$_2$/g-C$_3$N$_4$ nanocomposites has higher MB adsorption effect. The comparison of $q_{\text{max}}$ of different adsorbents is given in Table S3. Therefore, the adsorption capacity of MoS$_2$/g-C$_3$N$_4$ nanocomposites for MB was similar or higher than that of other commonly used adsorbents.

We use the separation coefficient $R_L$ to evaluate the feasibility of adsorption by the following equation:

$$R_L = \frac{1}{1+K_L C_0}$$

Where $C_0$ (mg/L) and $K_L$ (L/mg) had explained above. As shown in Table S4, we observed that $0 < R_L < 1$, it indicated that the process of MB adsorption was favorable (Mohammadnejad et al., 2018).

Table 1. Modeling parameters of adsorption isotherm calculated by Langmuir model and Freundlich model.
3.5 Adsorption thermodynamics

At different temperatures, we used various thermodynamic parameters to understand the adsorption process. The thermodynamic parameters can be obtained by the following expression:

\[
K_L = \frac{q_e}{C_e}
\]  

(9)

\[
\Delta G^\theta = -RT \ln K_L
\]  

(10)

\[
\ln K_L = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT}
\]  

(11)

Where \(K_L\) is the equilibrium distribution coefficient, \(R\) is the molar gas constant (8.314 J/mol \(\cdot\) K \(\cdot\) mol \(^{-1}\)), \(T\) (K) is the temperature, \(\Delta G^\theta\) is the Gibbs free energy change, \(\Delta H^\theta\) is the enthalpy change, \(\Delta S^\theta\) is entropy change. Figure 6 showed the plot of \(\ln K_L\) against 1/T. From Table 2 we can see that the value of \(\Delta G^\theta\) was negative, indicating that the adsorption process was a spontaneous process at different temperatures, and the increase in temperature was conducive to the adsorption of MB. The value of \(\Delta H^\theta\) was positive, indicating that the adsorption was an endothermic process. In addition, the value of \(\Delta S^\theta\) was positive which indicated that the disorder of the solid-liquid interface increases during the adsorption process.

Table 2. Thermodynamic parameters for adsorption of MB by MoS\(_2\)/g-C\(_3\)N\(_4\) nanocomposites.
3.6 Ecological assessment of treated wastewater

In order to evaluate the ecological characteristics of the treated MB solution, the untreated MB solution and the treated solution were used for the culture of wheat and chickpea seeds, respectively [24]. The growth of germinated wheat and chickpea seeds was analyzed in the next 15 days. As shown in Fig. 7a, the average length of wheat seedlings grown with MB solution is 14.7 cm, while that is 17.2 cm under treated solution. As shown in Fig. 7b, the average length of chickpea grown with MB solution is 21.4 cm, and that with treated solution is 43.6 cm. The results showed that MB solution had strong inhibition on root and bud germination of both plants. Compared with untreated MB solution, the treated solution shows a great improvement role for growth of root and bud parts of wheat and chickpea.

3.7 Adsorption mechanism

Figure S10 showed the possible adsorption mechanism of MoS$_2$/g-C$_3$N$_4$. From the above that the adsorption of MB by MoS$_2$/g-C$_3$N$_4$ belonged to Langmuir monolayer adsorption model. The adsorption rate decreased with the increase of adsorption capacity. From the molecular structure of MB and MoS$_2$/g-C$_3$N$_4$, there was an electrostatic interaction between MB and MoS$_2$/g-C$_3$N$_4$ due to that MB is a cationic dye, while MoS$_2$/g-C$_3$N$_4$ is negatively charged in the solution (Fig. S3). As shown in Figure S10, MB and MoS$_2$/g-C$_3$N$_4$ both contain aromatic rings and possible stronger π-π interaction. In addition, both MoS$_2$/g-C$_3$N$_4$ and MB contain nitrogen atoms, and hydrogen bonds may be formed between them. The above analysis indicated that the adsorption of MB was mainly driven by electrostatic interactions, together with π-π interaction and hydrogen bond.

4. Conclusions

We designed and synthesized MoS$_2$/g-C$_3$N$_4$ nanocomposites for MB adsorption in this study. The experimental results indicated that it is feasible to remove MB from water by adsorption. The factors affecting the adsorption performance of MB (pH of solution, adsorption dose, MB concentration and adsorption temperature) were studied. The adsorption process followed the Langmuir monolayer adsorption isotherm model and the pseudo second-order kinetic model. Thermodynamic data showed that adsorption is a spontaneous process, and the increase of temperature is conducive to the adsorption.
of MB. MB can reach the adsorption equilibrium within 60 min, and the maximum adsorption capacity of MB was 278.4 mg/g at 45 °C. On the other hand, after the treated wastewater was used for watering the seeds of wheat and chickpea, we found that the treated wastewater was more conducive to the growth of wheat and chickpea than MB solution. The present study indicated that the synthesized MoS$_2$/g-$\text{C}_3\text{N}_4$ nanocomposites have good application prospects for waste-water treatment and environmental remediation.

**Declarations**

*Ethics approval and consent to participate:* Not applicable

*Consent for publication:* Not applicable

*Declaration of interests:* The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

*Funding:* This research received no external funding

*Author Contributions:* Conceptualization, C.Q.; methodology, Z.W., J.H.; validation, C.Q., Z.W., J.H., N.C.; investigation, Z.W., J.H., J.W., C.Z, C.Q., N.C.; resources, C.Q., N.C.; data curation, Z.W., C.Q., J.H., C.Z., J.W., W.I., N.C.; writing-original draft preparation, Z.W., J.H., C.Q.; writing-review and editing, Z.W., J.H., C.Q., W.I.; supervision, C.Q., N.C.; project administration, C.Q., N.C.; funding acquisition, C.Q., N.C.

**Acknowledgments**

This work was financially supported by National Natural Science Foundation of China (21572180, 21602174), the Intergovernmental Science and Technology Cooperation and Exchange Program between China and Romania (43-24-20180510), the Natural Science Basic Research Plan in Shaanxi Province of China (2012JZ2002), and Academic Funding of Northwestern Polytechnical University (NPU, 17GH0402, W212002). We gratefully acknowledge the Analytical and Testing Center (ATC) of Northwestern Polytechnical University for providing well-support as SEM, TEM and XRD throughout the research work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at

**References**

1. Alarifi IM, Al-Ghamdi YO, Darwesh R, Ansari MO, Uddin MK (2021) Properties and application of MoS$_2$ nanopowder: Characterization, Congo red dye adsorption, and optimization. J Mater Res Technol 13:1169–1180. https://doi.org/10.1016/j.jmrt.2021.05.028
2. Ali GAM, Thalji MR, Soh WC, Algarni H, Chong KF (2019) One-step electrochemical synthesis of MoS$_2$/graphene composite for supercapacitor application. J Solid State Electrochem 24(1):25–34. https://doi.org/10.1007/s10008-019-04449-5

3. Cao YZ, Gao Q, Li Q, Jing XB, Wang SF, Wang W (2017) Synthesis of 3D porous MoS$_2$/g-C$_3$N$_4$ heterojunction as a high efficiency photocatalyst for boosting H$_2$ evolution activity. RSC Adv 7(65):40727–40733. https://doi.org/10.1039/c7ra06774g

4. Carolin CF, Kumar PS, Saravanan A, Joshiba GJ, Naushad M (2017) Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. J EnvironChem Eng 5(3):2782–2799. https://doi.org/10.1016/j.jece.2017.05.029

5. Chen L, Li YH, Du QJ, Wang ZH, Xia YZ, Yedinak E, Lou J, Ci LJ (2017) High performance agar/graphene oxide composite aerogel for methylene blue removal. Carbohydr Polym 155:345–353. https://doi.org/10.1016/j.carbpol.2016.08.047

6. Chen YX, Ma WJ, Cai KF, Yang XW, Huang CJ (2017) In Situ Growth of Polypyrrole onto Three-Dimensional Tubular MoS$_2$ as an Advanced Negative Electrode Material for Supercapacitor. Electrochim Acta 246:615–624. https://doi.org/10.1016/j.electacta.2017.06.102

7. Fang Y, Huang Q, Liu P, Shi J, Xu G (2018) Easy-separative MoS$_2$-glue sponges with high-efficient dye adsorption and excellent reusability for convenient water treatment. Coll Surf A: Physicochem Eng Aspects 540:112–122. https://doi.org/10.1016/j.colsurfa.2018.01.001

8. Farhat NM, Vrouwenvelder JS, Van Loosdrecht MCM, Bucs SS, Staal M (2016) Effect of water temperature on biofouling development in reverse osmosis membrane systems. Water Res 103:149–159. https://doi.org/10.1016/j.watres.2016.07.015

9. Fu NJ, Li LT, Liu X, Fu NA, Zhang CC, Hu LD, Li DH, Tang BK, Zhu T (2017) Specific recognition of polyphenols by molecularly imprinted polymers based on a ternary deep eutectic solvent. J Chromatogr A 1530:23–34. https://doi.org/10.1016/j.chroma.2017.11.011

10. Gao Y, Guo Y, Zhang H (2016) Iron modified Bentonite: Enhanced adsorption performance for organic pollutant and its regeneration by heterogeneous visible light photo-Fenton process at circumneutral pH. J Hazard Mater 302:105–113. https://doi.org/10.1016/j.jhazmat.2015.09.036

11. Guan T, Fang L, Lu Y, Wu F, Ling FL, Gao JM, Hu BS, Meng FM, Jin XQ (2017) A facile approach to synthesize 3D flower-like hierarchical NiCo layered double hydroxide microspheres and their enhanced adsorption capability. Coll Surf A: PhysicochemEng Aspects 529:907–915. https://doi.org/10.1016/j.colsurfa.2017.06.049

12. GunTure, Aggarwal R, Garg AK, Kaushik J, Sonkar SK (2020) Pollutant-based onion-like nanocarbons for improving the growth of gram plants. Mater Today Chem, 18, Article 100352. https://doi.org/10.1016/j.mtchem.2020.100352

13. GunTure, Kaushik J, Garg AK, Saini D, Khare P, Sonkar SK (2020) Pollutant Diesel Soot Derived Onion-like Nanocarbons for the Adsorption of Organic Dyes and Environmental Assessment of Treated Wastewater. Indust Eng Chem Res 59(26), 12065–12074. https://doi.org/10.1021/acs.iecr.0c01267
14. Gunture, Singh A, Bhati A, Khare P, Tripathi KM, Sonkar SK (2019) Soluble Graphene Nanosheets for the Sunlight-Induced Photodegradation of the Mixture of Dyes and its Environmental Assessment. Sci Rep 9:Article 2522. https://doi.org/10.1038/s41598-019-38717-1

15. Hu R, Wang X, Dai S, Shao D, Hayat T, Alsaedi A (2015) Application of graphitic carbon nitride for the removal of Pb(II) and aniline from aqueous solutions. Chem Eng J 260:469–477. https://doi.org/10.1016/j.cej.2014.09.013

16. I M, Saleh HAM, Qasem KMA, Shahid M, Mehtab M, Ahmad M (2020) Efficient and selective adsorption and separation of methylene blue (MB) from mixture of dyes in aqueous environment employing a Cu(II) based metal organic framework. Inorg Chim Acta, 511, Article 119787. https://doi.org/10.1016/j.ica.2020.119787

17. Jun YS, Lee EZ, Wang XC, Hong WH, Stucky GD, Thomas A (2013) From Melamine-Cyanuric Acid Supramolecular Aggregates to Carbon Nitride Hollow Spheres. Adv Funct Mater 23(29):3661–3667. https://doi.org/10.1002/adfm.201203732

18. Katheresan V, Kansedo J, Lau SY (2018) Efficiency of various recent wastewater dye removal methods: A review. J Environ Chem Eng 6(4):4676–4697. https://doi.org/10.1016/j.jece.2018.06.060

19. Li ZZ, Meng XC, Zhang ZS (2018) Recent development on MoS$_2$-based photocatalysis: A review. J Photochem Photobiol C-Photochem Rev 35:39–55. https://doi.org/10.1016/j.jphotochemrev.2017.12.002

20. Lin B, Li J, Xu B, Yan X, Yang B, Wei J, Yang G (2019) Spatial positioning effect of dual cocatalysts accelerating charge transfer in three dimensionally ordered macroporous g-C$_3$N$_4$ for photocatalytic hydrogen evolution. Appl Catal B: Environ 243:94–105. https://doi.org/10.1016/j.apcatb.2018.10.029

21. Liu C, Wang QM, Jia FF, Song SX (2019) Adsorption of heavy metals on molybdenum disulfide in water: A critical review. J Mol Liquids, 292, Article 111390. https://doi.org/10.1016/j.molliq.2019.111390

22. Liu Z, Chen G, Hu F, Li X (2020) Synthesis of mesoporous magnetic MnFe$_2$O$_4$@CS-SiO$_2$ microsphere and its adsorption performance of Zn$^{2+}$ and MB studies. J Environ Manage 263:Article 110377. https://doi.org/10.1016/j.jenvman.2020.110377

23. Manilo M, Lebovka N, Barany S (2016) Mechanism of Methylene Blue adsorption on hybrid laponite-multi-walled carbon nanotube particles. J Environ Sci 42:134–141. https://doi.org/10.1016/j.jes.2015.06.011

24. Mohammadnejad M, Hajiashrafi T, Rashnavadi R (2018) An erbium-organic framework as an adsorbent for the fast and selective adsorption of methylene blue from aqueous solutions. J Porous Mater 25(3):761–769. https://doi.org/10.1007/s10934-017-0489-8

25. Monga D, Ilager D, Shetti NP, Basu S, Aminabhavi TM (2020) 2D/2D heterojunction of MoS$_2$/g-C$_3$N$_4$ nanoflowers for enhanced visible-light-driven photocatalytic and electrochemical degradation of organic pollutants. J Environ Manage 274:Article 111208. https://doi.org/10.1016/j.jenvman.2020.111208
26. Murray A, Ormeci B (2018) Competitive effects of humic acid and wastewater on adsorption of Methylene Blue dye by activated carbon and non-imprinted polymers. J Environ Sci 66:310–317. https://doi.org/10.1016/j.jes.2017.04.029

27. Oladipo AA, Gazi M (2014) Enhanced removal of crystal violet by low cost alginate/acid activated bentonite composite beads: Optimization and modelling using non-linear regression technique. J. Water Proc. Eng. 2, 43–52. https://doi.org/10.1016/j.jwpe.2014.04.007

28. Pan Y, Wang J, Sun C, Liu X, Zhang H (2016) Fabrication of highly hydrophobic organic–inorganic hybrid magnetic polysulfone microcapsules: A lab-scale feasibility study for removal of oil and organic dyes from environmental aqueous samples. J Hazard Mater 309:65–76. https://doi.org/10.1016/j.jhazmat.2016.02.004

29. Pang H, Huang S, Wu Y, Yang D, Wang X, Yu S, Chen Z, Alsaedi A, Hayat T, Wang X (2018) Efficient elimination of Uvi by polyethyleneimine-decorated fly ash. InorgChemFront 5(10):2399–2407. https://doi.org/10.1039/c8qi00253c

30. Tehrani MS, Zare-Dorabei R (2016) Competitive removal of hazardous dyes from aqueous solution by MIL-68(Al): Derivative spectrophotometric method and response surface methodology approach. Spectrochim Acta Part A-Mol Biomol Spectro 160:8–18. https://doi.org/10.1016/j.saa.2016.02.002

31. Wang C-Y, Zeng W-J, Jiang T-T, Chen X, Zhang X-L (2019) Incorporating attapulgite nanorods into graphene oxide nanofiltration membranes for efficient dyes wastewater treatment. Sep Purif Technol 214:21–30. https://doi.org/10.1016/j.seppur.2018.04.079

32. Wang C, Jiang X, Zhou L, Xia G, Chen Z, Duan M, Jiang X (2013) The preparation of organo-bentonite by a new gemini and its monomer surfactants and the application in MO removal: A comparative study. Chem Eng J 219:469–477. https://doi.org/10.1016/j.cej.2013.01.028

33. Wu HJ, Li CM, Che HN, Hu H, Hu W, Liu CB, Ai JZ, Dong HJ (2018) Decoration of mesoporous Co$_3$O$_4$ nanospheres assembled by monocrystal nanodots on g-C$_3$N$_4$ to construct Z-scheme system for improving photocatalytic performance. Appl Surf Sci 440:308–319. https://doi.org/10.1016/j.apsusc.2018.01.134

34. Yi S-S, Yan J-M, Wulan B-R, Li S-J, Liu K-H, Jiang Q (2017) Noble-metal-free cobalt phosphide modified carbon nitride: An efficient photocatalyst for hydrogen generation. Appl Catal B: Environ 200:477–483. https://doi.org/10.1016/j.apcatb.2016.07.046

35. Yu S, Yin L, Pang H, Wu Y, Wang X, Zhang P, Hu B, Chen Z, Wang X (2018) Constructing sphere-like cobalt-molybdenum-nickel ternary hydroxide and calcined ternary oxide nanocomposites for efficient removal of U(VI) from aqueous solutions. Chem Eng J 352:360–370. https://doi.org/10.1016/j.cej.2018.07.033

36. Zanacic E, Stavrinides J, McMartin DW (2016) Field-analysis of potable water quality and ozone efficiency in ozone-assisted biological filtration systems for surface water treatment. Water Res 104:397–407. https://doi.org/10.1016/j.watres.2016.08.043

37. Zhang Y, Zhou Z, Shen Y, Zhou Q, Wang J, Liu A, Liu S, Zhang YM (2016) Reversible Assembly of Graphitic Carbon Nitride 3D Network for Highly Selective Dyes Absorption and Regeneration. ACS
38. Zhao L, Lv W, Hou J, Li Y, Duan J, Ai S (2020) Synthesis of magnetically recyclable g-C₃N₄/Fe₃O₄/ZIF-8 nanocomposites for excellent adsorption of malachite green. Microchem J 152:Article 104425. https://doi.org/10.1016/j.microc.2019.104425

39. Zhao S, Fang J, Wang Y, Zhang Y, Zhou Y, Zhuo S (2020) Synthesis of carbon nitride hollow microspheres with highly hierarchical porosity templated by poly (ionic liquid) for photocatalytic hydrogen evolution. Appl Organometal Chem 34(4), Article e5474. https://doi.org/10.1002/aoc.5474

40. Zhu SJ, Xu YP, Zhu ZG, Liu ZQ, Wang W (2020) Activation of peroxymonosulfate by magnetic Co-Fe/SiO₂ layered catalyst derived from iron sludge for ciprofloxacin degradation. Chem Eng J 384:Article 123298. https://doi.org/10.1016/j.cej.2019.123298

Figures

Figure 1

XRD patterns of g-C₃N₄, MoS₂/g-C₃N₄ and MoS₂.
Figure 2

(a) XPS survey scanning of MoS2/g-C3N4. XPS spectra of (b) C 1s, (c) N 1s, (d) Mo 3d and (e) S 2p.
Figure 3

FESEM images of (a) MCA, (b) g-C3N4, (c) MoS2 and (d) MoS2/g-C3N4. HRTEM images of (e-f) MoS2/g-C3N4.
Figure 4

The influence of contact time (a), linear fitted pseudo-first-order model (b), linear fitted pseudo-second-order model (c) and intra-particle diffusion model (d) for MB adsorption by MoS2/g-C3N4 nanocomposites (MB concentration: 100 mg/L, MB volume: 50 ml, adsorbent amount: 25 mg, temperature: 25 °C).
Figure 5

Linear fitted adsorption isotherm models of MB by MoS2/g-C3N4 nanocomposites at different temperatures: (a) Langmuir and (b) Freundlich (MB volume: 50 ml, adsorbent amount: 10 mg).

Figure 6

Linear fitted thermodynamic plot for MB adsorption (MB volume: 50 ml, adsorbent amount: 10 mg).
Figure 7

Effect of MB and treated wastewater obtained after adsorption by MoS2/g-C3N4 nanocomposites on (a) wheat plants and (b) Chickpea plants (MB concentration 40 mg L\(^{-1}\); MoS2/g-C3N4 nanocomposites loading 10 mg).
Figure 8

Scheme 1. Schematic diagram for the flower-like MoS2/g-C3N4 preparation.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Graphicabstract.docx
- SI20210916.pdf