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Effect of Synthesis Method and Reaction Conditions on ciprofloxacin adsorption from aqueous solutions by MoS_2 Materials

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Abstract: This study investigates the adsorption performance of MoS_2 nanomaterials under various conditions for the removal of ciprofloxacin (CIP) from water. Antibiotics are essential for treating infections, but their persistence in water and the resulting antibiotic resistance pose environmental risks. CIP is commonly found in water systems, necessitating effective removal methods. MoS_2, a material that has garnered significant attention in recent years, is widely used across various fields and shows promising characteristics as an adsorbent. In this experiment, the adsorption performance of commercial molybdenum disulfide was compared with hydrothermally synthesized MoS_2 nanomaterials, with structural analysis conducted using XRD and SEM. The results demonstrated that the synthesized MoS_2 nanomaterials, with smaller particle sizes, exhibited more stable and rapid CIP adsorption, fitting well with a pseudo-second-order kinetic model. These findings suggest that MoS_2 nanomaterials are effective and stable adsorbents for CIP removal from water.

Keywords: Ciprofloxacin, Molybdenum disulfide, adsorbents, Water treatment

1. INTRODUCTION

Antibiotics are a diverse class of drugs, both synthetic and naturally occurring, designed to combat various infectious diseases in humans and animals[1]. Their widespread use in medical treatments has significantly improved healthcare outcomes[2]. However, the discharge of antibiotics into natural water bodies, including domestic, industrial, and medical wastewater, poses serious risks to human safety[3]. The persistent presence and bioaccumulation of antibiotics in the environment contribute to the proliferation of antibiotic-resistant bacteria, leading to incurable and life-threatening diseases[4].On April 30, 2014, the World Health Organization (WHO) released a report indicating the global spread of antibiotic-resistant bacteria. Based on data from 114 countries, WHO found cases of cephalosporin antibiotics being ineffective in treating gonorrhea in countries like Japan, France, and South Africa. Ciprofloxacin (CIP) is among the most frequently detected antibiotics in multiple water systems[5]. Therefore, there is a critical need for effective treatment technologies to reduce CIP from water environment.

Current methods for CIP removal include photocatalytic degradation[6], ozonation[7], biodegradation[8], and adsorption techniques[9]. Photocatalytic degradation utilizes light energy to catalyze the oxidation of ciprofloxacin, breaking it down into harmless byproducts. Ozonation involves the use of ozone to decompose ciprofloxacin molecules, reducing their pollution potential[10]. Biodegradation employs microorganisms to break down ciprofloxacin into non-toxic substances[11]. Adsorption, a common physical-chemical method, uses solid adsorbents like activated carbon, nanoscale zero valent iron[12] and various natural materials[13] to capture pollutants molecules from water by their porous structures[14], safeguarding aquatic life and human health[15].

MoS_2 is a novel nanomaterial with a graphene-like two-dimensional (2D) layered and hexagonal crystal structure[16]. Its high surface area, chemical stability, and tunable surface properties make it a promising candidate for adsorption-based water treatment processes. Study investigated that MoS_2 achieved an impressive 96% removal efficiency for rhodamine-B dye and exhibited highly effective removal of antibiotics[17]. Furthermore, MoS_2 maintained its adsorption capacity even after multiple reuse cycles, showcasing its potential as a sustainable adsorbent in water treatment applications[18].

The unique layered and porous structure, along with its physical adsorption properties, enables MoS_2 to be efficiently reusable. Its good dispersibility in aqueous environments and

resistance to oxidation offer superior stability, cost-effectiveness, and efficiency compared to traditional adsorbents. These characteristics have garnered significant interest in recent years as a water treatment adsorbent. This study aims to ßelucidate the influence of synthesis techniques on the characteristics and adsorption properties of MoS_2, and evaluate its effectiveness in removing ciprofloxacin under various conditions.

2. MATERIALS AND METHODS

2.1 Materials

Ciprofloxacin hydrochloride monohydrate ($C_{17}H_{18}FN_3O_3 \cdot HCl \cdot H_2O$) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Ammonium molybdate tetrahydrate ([$(NH_4)6Mo_7O_{24} \cdot 4H_2O$], 99%) and thiourea ($CH_4N_2S$, 99%) were sourced from Sigma-Aldrich. All solvents used in this study were deionized water.

2.2 Synthesis of MoS_2

To synthesize molybdenum disulfide (MoS_2), specific concentrations of molybdenum (Mo) and sulfur (S) precursors were combined in a solvent, such as ultra-pure water. The mixture was magnetically stirred until all chemicals were completely dissolved. The resulting solution was then put into a Teflon-lined stainless-steel autoclave, which was subsequently sealed and placed in an oven at 160°C for 24 hours. During this hydrothermal treatment, MoS_2 was produced according to the following reaction equation:

$$CH_4N_2S + 2H_2O \rightarrow 2NH_3 + CO_2 + H_2S$$
$$4Na_2MoO_4 + 9H_2S + 6HCl \rightarrow 4MoS_2 + Na_2SO_4 + 12H_2O + 6NaCl$$

Following the thermal treatment, the autoclave was cooled naturally under room temperature. The black MoS_2 powder formed was collected using a vacuum filtration system. The obtained MoS_2 powder needs to be washed by ultra-pure water and ethanol for three times to remove residual impurities. Finally, the cleaned MoS_2 powder was dried under vacuum at 80°C for 24 hours.

2.3 Batch experiments

MoS_2 suspension was prepared by 0.125g of MoS_2 and 5ml of deionized water (DIW) , then use ultrasonic water bath sonication for 30 minutes at 40 degrees Celsius to help to achieve a uniformly dispersed suspension.

Dissolving 25.618 mg of CIP in 1000 ml of DIW in a 1000ml volumetric flask to prepare 22mg/L ciprofloxacin solution.

Batch tests using 5 ml of the MoS_2 suspension and 45ml of the ciprofloxacin solution to form a reaction solution with an initial ciprofloxacin concentration of 20 mg/L and an adsorbent concentration of 0.5 g/L, to investigate the CIP removal performance between different MoS_2 materials under various dosage, pH, temperature and initial concentration experiment conditions. The flasks with reaction solution were placed on a magnetic stirrer under1000 rpm for two hours. Samples were taken using a syringe and filtered through a 0.45 μm filter at intervals of 10, 20, 40, 60, 80, and 120 minutes. And then collect liquid in 2ml centrifuge tubes for storage and further analysis.

2.4 Analytical instruments

The remaining CIP concentration after the treatment was measured using a UV-vis spectrophotometer (UV-1280, SHIMADZU, Japan) within the wavelength range of 255-290 nm. Before measuring the CIP concentration, the UV-1280 was calibrated using standard solutions with concentrations of 0, 0.25, 0.5, 0.75, 1, 2, 3, 4, and 5 mg L^-1. The calibration curve for the UV-1280 is described by the following equation:

$$Y=0.1151X+0.0028 \quad (1)$$

where Y represents the absorbance value at 275 nm, and X is the CIP concentration in mg L^-1.

The characterization of MoS_2 was performed using SEM and XRD. These techniques were utilized to analyze the surface morphology, elemental composition, and crystalline structure of the MoS_2 samples.

2.5 Evaluation of the performance of MoS2

The competence of MoS_2 particles was assessed by calculating the final removal efficiency (RE) using the following equation:

$$RE\ (\%) = ((Ci-Cf)/Ci)\times 100\% \quad (2)$$

Ci is CIP initial concentration (mg·L-1) and Cf is CIP final concentration (mg·L-1).

3. RESULTS AND DISCUSSION

3.1 Characterization of MOS_2

Figure 3-1 shows the SEM images of two types of MoS_2 nanomaterials. C-MoS_2 exhibits a sheet-like structure, with these sheets irregularly stacked together to form a layered plate-like morphology. In contrast, MoS_2 displays a flower-like structure composed of many tiny spherical structure nanomaterials. This flower-like structure suggests that MoS_2 material may have a higher surface area and better adsorption properties. These different structural characteristics reflect the significant impact of different synthesis methods and conditions on the morphology of MoS_2 nanomaterials and may lead to performance differences in practical applications.

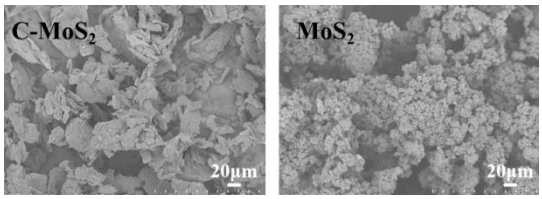

Fig. 3-1. SEM observation of (a) C-MoS_2, (b) S-MoS_2.

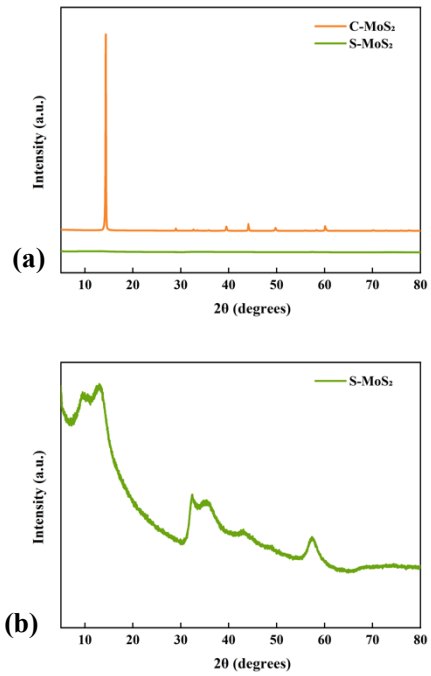

Fig. 3-2.XRD patterns of (a) C-MoS_2, (b) S-MoS_2.

The XRD pattern of C-MoS_2 shows a very strong peak at 14.34°, corresponding to the (002) plane of MoS_2, indicating its interlayer spacing and highly ordered layered structure. On the other hand, the XRD pattern of the synthesized MoS_2 nanomaterials reveals the 2H-phase structure. The broad and weak peaks may be due to the synthesized MoS_2 having smaller crystallite size and/or higher amorphousness. These differences reflect distinct structural characteristics between the two materials.

3.2 Adsorption Performance

3.2.1 Effect of Contact Time on CIP Removal

Figure 3-3 presents the adsorption kinetics of CIP onto two types of MoS_2 nanomaterials. This figure is used to study the changes in the adsorption process over time. The x-axis represents time (minutes), while the y-axis represents the ratio of CIP concentration to the initial concentration. As shown in the figure, the adsorption amount of CIP for both materials increases rapidly in the initial stage, then gradually levels off, eventually reaching adsorption equilibrium at approximately 60 minutes. However, the commercial MoS_2 shows a desorption trend after reaching equilibrium, whereas the synthesized MoS_2 remains relatively stable.

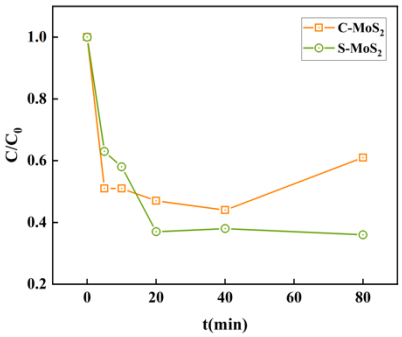

Fig.3-3.Adsorption kinetics curves of ciprofloxacin (CIP) on C-MoS_2 and S-MoS_2.

The fitting of first order and second-order kinetic models is commonly used to conduct in-depth studies of the adsorption mechanisms of materials[19]. As illustrated in the **figure 3-4**, the pseudo-second-order kinetic model fits the adsorption kinetics of contaminants on MoS_2 very well, with the maximum regression correlation coefficient values (R^2) of 0.97 and 0.99, respectively.

In summary, the adsorption rate of CIP on MoS_2 materials is faster in the initial stage, possibly due to the abundance of vacant and active sites. Over time, these sites are gradually occupied, the adsorption rate slows down, and equilibrium is eventually reached. The fitting curves indicate that the pseudo-second-order kinetic model better describes the adsorption process.

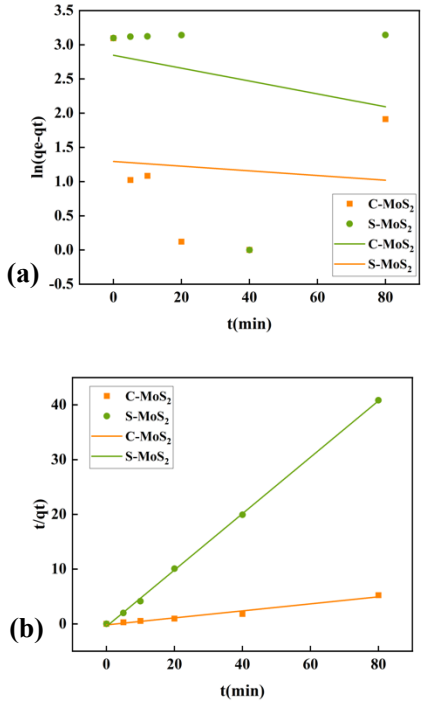

Fig. 3-4. Pseudo-first-order and pseudo-second-order kinetic model fittings for the adsorption of CIP on (a) C-MoS_2, (b) S-MoS_2.

3.2.2 Effect of Adsorbent Dosages on CIP Removal

To assess the effectiveness of commercial MoS_2 and MoS_2 nanoadsorbents in removing ciprofloxacin (CIP) contaminants, an adsorption batch experiment was performed using varying concentrations of the adsorbents. The dosage tested were 0.25 g/L, 0.5 g/L, 0.75 g/L, and 1 g/L. In this experiment, 5 mL of each adsorbent concentration was added to 45 mL of a batch solution with a CIP concentration of 22 mg/L. The mixtures were allowed to react for 2 hours to ensure sufficient interaction. After the reaction period, the removal efficiency for CIP was determined for each dosage. **Figure 3-5** presents the CIP removal efficiencies for the different dosages of the two types of MoS_2 adsorbents.

The removal efficiency of both adsorbents for CIP increased with higher dosages, reaching a peak at a dosage of 0.75 g/L, after which the efficiency began to decline. At the optimal dosage of 0.75 g/L, the removal efficiency of commercial MoS_2 for CIP was 25.98%, while that of S-MoS_2 was significantly higher at 79.48%, over three times that of the commercial MoS_2. Overall, the synthesized MoS_2 demonstrated superior CIP removal capabilities, which can likely be attributed to its unique two-dimensional structure.

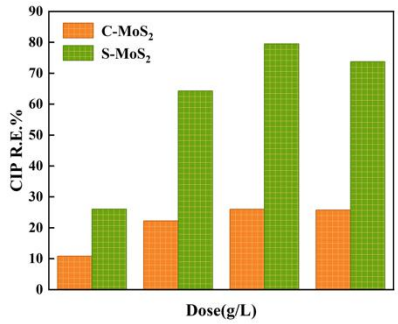

Fig. 3-5.Effect of adsorbent dosages on CIP removal by C-MoS_2 and S-MoS_2.

3.2.3 Effect of pH on CIP Removal

The effect of pH on the adsorption of CIP by MoS_2 was studied over a wide pH range (3-9), with the concentration distribution shown in **Figure 3-6**. Both adsorbents exhibited distinct and individual characteristics under different pH conditions.

The removal efficiency of CIP by both C-MoS_2 and S-MoS_2 adsorbents was significantly influenced by the pH, as shown in Figure 3-2. The synthesized MoS_2 consistently demonstrated superior performance across the pH range of 3 to 10. At a lower pH of 3, the synthesized MoS_2 achieved a removal efficiency of around 52%, compared to the 22.9% efficiency of commercial MoS_2. The efficiency peaked at pH 10 for synthesized MoS_2, reaching approximately 76.88%, whereas commercial MoS_2 peaked at pH 7 with a 36.73% efficiency. Overall, the synthesized MoS_2 outperformed the commercial counterpart at all pH levels, with optimal performance observed in slightly alkaline conditions.

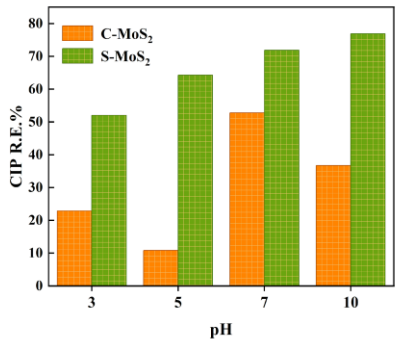

Fig. 3-6.Effect of pH on CIP removal by C-MoS_2 and S-MoS_2.

3.2.4 Effect of Temperature on CIP Removal

The effect of temperature on the removal efficiency of ciprofloxacin by commercial MoS_2 and synthesized MoS_2 adsorbents is depicted in **figure 3-7**. The CIP removal efficiency was

evaluated at five different temperatures: 15°C, 25°C, 45°C, 55°C, and 65°C.

Both adsorbents exhibit temperature-dependent removal efficiencies, with the synthesized MoS_2 showing a more pronounced variation across the temperatures. The synthesized MoS_2 consistently outperforms the commercial MoS_2 at all temperatures tested, demonstrating its superior adsorption capability for CIP. The optimal temperature for CIP removal by synthesized MoS_2 is 45°C, where it achieves the highest efficiency of about 65%. For commercial MoS_2, there is no significant peak, but the highest efficiency observed is at 15°C and 65°C with approximately 30%.

The synthesized MoS_2 exhibits excellent adsorption properties across a range of temperatures, with particularly high performance at 45°C. This superior performance can be attributed to the unique structure of the synthesized MoS_2, which provides a larger surface area and more active sites for CIP adsorption. In contrast, the commercial MoS_2 shows lower and more variable efficiencies, indicating its comparatively inferior adsorption capabilities. These results suggest that the synthesized MoS_2 is more effective and reliable over a range of environmental conditions.

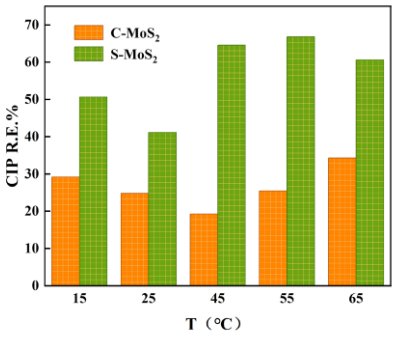

Fig. 3-7.Effect of temperature on CIP removal by C-MoS_2 and S-MoS_2.

3.2.5 Effect of Initial Concentration on CIP Removal

Initial concentration is an important factor affecting adsorption efficiency[20].The effect of initial concentration on CIP removal using MoS_2 was evaluated. As shown in the **figure 3-8**, MoS_2 consistently exhibited higher removal efficiencies than C-MoS_2 across all tested initial concentrations (10, 20, 50, 70, and 100 mg/L).

At 10 mg/L, MoS_2 achieved a removal efficiency of approximately 70.1%, compared to 29.01% for C-MoS_2. As the initial concentration increased to 20 mg/L, MoS_2's efficiency slightly decreased to about 60%, while C-MoS_2's efficiency dropped to around 20%. At 50 mg/L, the efficiencies were 40% for MoS_2 and 10% for C-MoS_2. At the highest concentrations (70 mg/L and 100 mg/L), both materials showed reduced efficiencies, with S-MoS_2 around 10% and C-MoS_2 near negligible. In conclusion, MoS_2 demonstrate significant potential as an effective adsorbent for CIP removal, outperforming commercial MoS_2, especially at lower initial concentrations.

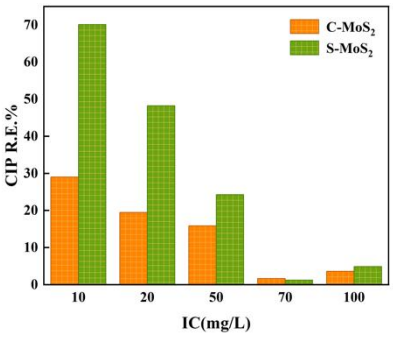

Fig. 3-8.Effect of initial concentration on CIP removal by C-MoS_2 and S-MoS_2.

4. CONCLUSION AND OUTLOOK

This study aimed to explore the efficiency of commercial MoS_2 and synthesized MoS_2 in removing CIP from wastewater under varying conditions of pH and temperature. The synthesized MoS_2 adsorbent was produced using a modified green hydrothermal method, and its structural and morphological properties were characterized using various analytical techniques, including XRD, SEM and UV-vis analysis.

The experimental results demonstrated that the synthesized MoS_2 exhibited superior adsorption performance compared to the commercial MoS_2 across different pH levels and temperatures. Specifically, the synthesized MoS_2 showed the highest CIP removal efficiency at pH 9 and 45°C, reaching approximately 76.88% and 67.88%, respectively. The adsorption kinetics followed a pseudo-second-order model, indicating rapid adsorption rates.

Based on these findings, the synthesized MoS_2 proves to be a promising non-conventional adsorbent for CIP removal in water treatment applications. Future research should focus on optimizing the synthesis process to enhance the structural properties and cost-effectiveness[21] of MoS_2. Investigating the regeneration and desorption processes is crucial for developing acost-effective recycling strategy[22]. Additionally, using simulations[23] and modeling[24] to enhance practical applications and testing the synthesized MoS_2 on other contaminants and real wastewater samples will further validate its potential in environmental remediation.

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