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Green Synthesis of A Novel MXene–CS Composite Applied in Treatment of Cr(VI) Contaminated Aqueous Solution

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Abstract: The considerable amount of Cr(VI) pollutants in the aqueous environment is a significant environmental concern that cannot be ignored. A series of novel Mxene–CS inorganic–organic composite nanomaterials synthesized by using the solution reaction method was applied to treat the Cr(VI) contaminated water. The Mxene–CS composites were characterized through SEM (scanning electron microscope), XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), and FTIR (Fourier transform infrared). The XRD patterns (observed at 2θ of 18.1° , 35.8° , 41.5° , and 60.1°) and the FT–IR spectra ($-\text{NH}_2$ group for 1635 and 1517 cm^{-1} , and $-\text{OH}$ group for 3482 cm^{-1}) illustrated that CS was successfully loaded on the Mxene. The effects of solution pH, the dosage of Mxene–CS, and duration time on the adsorption of Cr(VI) by synthesized Mxene–CS were investigated. The removal efficiency of Cr(VI) was increased from 12.9% to 40.5% with Mxene–CS dosage ranging from 0.02 to 0.12 g/L. The adsorption process could be well fitted by the pseudo–second–order kinetics model, indicating chemisorption occurred. The Langmuir isotherm model could be better to describe the process with a maximum adsorption capacity of 43.1 mg/g. The prepared novel Mxene–CS composite was considered as an alternative for adsorption of heavy metals from wastewater.

Keywords: Mxene–CS composite; Cr(VI) contaminated aqueous solution; Green Synthesis; treatment of wastewater; heavy metals

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1. Introduction

Currently, with more rapid development of industrialization, more heavy metals in wastewater are derived from various industrial processes, such as mining, smelting, electroplating, tanning, and electrochemistry [1,2]. The heavy metals in wastewater would inevitably cause serious damage to the surface water, groundwater, and soil without proper treatment [2]. Among the reported heavy metals in wastewater, Cr(VI) is one of the most frequently detected in the natural environment, which was mainly derived from the chromium salt production and consumption process. The main existing oxidation states of Cr element in aqueous solution were Cr(III) and Cr(VI). The Cr(III) is a necessary trace element in our human body that is less harmful to the human body, compared with Cr(VI) [3,4]. Thus, more attention has been given to the treatment of Cr(VI)–polluted water/soil environment due to its potential threat to the ecological environment and human health [5]. Several methods have been proposed and investigated to remove Cr(VI) from

the water environment, including the adsorption method [6–9], reduction method [10], electrolysis method [11], ion exchange method [12], and membrane separation method [13]. Among the above-mentioned methods, the adsorption route has many inherent advantages for its lower energy consumption and relatively higher removal performance.

Chitosan (CS) is a kind of natural high molecular compound generating in the deacetylation of chitin. The CS is colorless and odorless, environmentally friendly with relatively higher adsorption properties [14] and stronger flocculation effect [15], that has already been widely applied in the chemical environmental protection [16,17], food hygiene [18,19], biomedicine [20], papermaking [21], and textile industries [22]. What is more, the hydroxyl group or amino group in the CS molecular would be beneficial to remove other pollutants for it can form into a hydrogen bond with a dye molecule (containing a -N=N- structure) or combine with the heavy metal ions under certain conditions [23]. However, the CS is not structurally stable under the acidic pH condition for it would degrade slowly in the acid solution, resulting in a decrease in the viscosity and molecular weight of the CS [24]. Therefore, the application of CS in the wastewater is obviously restricted for its unstable structure, while we should pay more attention to improve the stability of the CS and correspondingly increase its removal performance of pollutants from wastewater [25]. Several routes, including carboxymethylation modification [26], alkylation modification [27], and quaternization modification [27], etc., have been introduced to modify the structure of CS. A novel magnetic CS composite adsorbent was synthesized by the sol-gel method, proving its adsorption capacity of Cu^{2+} by the composite adsorbent could reach up to 216.6 mg/g [28]. The three-dimensional graphene oxide-CS composite was prepared and applied in adsorption of Uranium(VI) with an adsorption capacity of 384.6 mg/g at a pH of 8.3 [29].

The transition metal carbide or nitride (Mxene) is a kind of two-dimensional (2D) graphene-like nanomaterial newly developed in recent years [30]. Generally, the Mxene is mainly referred to as the transition metal carbides, nitrides, or borides, with the formula of $M_{n+1}X_nT_x$. In the formula, M is presenting the transition metal, X presents the non-metallic, including elements of carbon, nitrogen, and boron, T is presenting the functional groups (including -F, -O, and -OH) [31–33]. The novel Mxene phase is obtained by exfoliating the “A” component of the MAX phase in the HF solution, while the A in the MAX is presenting the elements for the Group IIIA or IVA, and X refers to the element of C or N [34]. The Mxene has been used as the adsorbent for the removal of heavy metal ions [35,36] or organic molecules [37] from the aqueous solution. The Mxene material is of relatively high structural stability, which should support and improve the structural stability of the CS [33]. It should be reasonable to expect the composite of Mxene and CS should be an ideal choice for the treatment of Cr(VI) contaminated water.

Herein, we synthesize and report a novel composite material of Mxene-CS. To the best of our knowledge, this is the first attempt to synthesize the Mxene-CS composite materials and used in the removal of Cr(VI) from the aqueous solution. We have studied the effects of pH, the Mxene-CS dosage, and the reaction time on the adsorption performance of Cr(VI) by synthesized Mxene-CS.

2. Experimental Section

2.1. Materials

The raw materials of Ti_3AlC_2 powders (One of MAX for the preparation of Mxene) were purchased from Ningbo Jinlei Nano Material Technology Co., Ltd., Zhejiang, China. The CS (≥ 95 wt % purity) was brought from Zhengzhou Paini Chemical reagent Co., Ltd., Henan, China. The HF was purchased from Luoyang Chemical Reagent Factory, Henan, China. The acetic acid was supplied by Tianjin Sailboat Chemical Reagent Technology Co., Ltd., Tianjin, China.

2.2. Synthesis of the Mxene–CS Composite

The novel Mxene–CS composite was prepared by the solution synthesis route. Firstly, the raw materials of Ti_3AlC_2 powders were passed through 400 mesh and then dissolved into the HF solutions (40% *w/w* water solution) in a PTFE beaker to obtain the mixed slurry (note that the HF is a dangerous inorganic acid, which would easily corrode the experimenter or the labware material). Then, the slurry was stirred in a magnetic stirrer (250 rpm) under room temperature for 96 h, followed by withdrawn and centrifugal filtration with deionized water until the pH of the suspension was neutral. The black liquid containing MXene was dried at 60 °C in a vacuum drying oven to obtain the dry MXene. The CS (0.82 g) was added into the 150 mL of acetic acid (5% *w/w* water solution) to obtain the mixed slurry, while the Mxene (0.82 g) was added into the mixed slurry and ultrasonically dispersed for 30 min. The obtained gelatinous product was withdrawn and placed in a vacuum oven at 60 °C to get the MXene–CS. Finally, the prepared MXene–CS composites were ground and passed through 20–60 mesh sieves, and stored for the adsorption experiments.

2.3. Material Characterization

The surface morphology of prepared MXene–CS composite was measured by scanning electron microscopy (SEM, Zeiss AURIGA CrossBeam Focused Ion Beam Electron Microscope, Baden–Württemberg, Germany). The powder XRD patterns of the prepared composite were determined by using an X-ray diffractometer (Empyrean, Panaco, Almelo, The Netherlands). The FT–IR spectra of CS, Mxene and the synthesized Mxene–CS were determined by using the spectrometer (TENSOR27, Bruker, Karlsruhe, Germany). The chemical states for the main elements, including Cr, Ti, and C, were measured by XPS analysis (Thermo Scientific Escalab 250Xi, New York, NY, USA). The Zeta potential of the Mxene–CS in the aqueous solution at the pH ranging from 2 to 12 was measured by using a Zeta potentiometer (JS94H, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., ShangHai, China).

2.4. Adsorption of Cr(VI) by Synthesized Mxene–CS

The stock solution of 1000 mM Cr(VI) was prepared by dissolving a certain amount of $\text{K}_2\text{Cr}_2\text{O}_7$ into the deionized water, then diluted into certain concentrations for the batch experiment. During the batch adsorption experiments, the $\text{K}_2\text{Cr}_2\text{O}_7$ solution (100 mL) was mixed with the Mxene–CS in a 250 mL Erlenmeyer flask, and oscillated in a horizontal shaking bath to control the temperature. The concentrations of Cr(VI) in the solution before and after the adsorption process were determined by using the diphenyl carbohydrazide spectrophotometric method at a wavelength of 540 nm [38]. The effect of reaction parameters, including the Mxene–CS dosage (0.02, 0.04, 0.06, 0.08, 0.1, and 0.12 g/L), the contact time (30, 60, 120, 180, 240, 300, 360, 480, 720, 960, 1200, and 1440 min), the temperature (25, 35, and 45 °C), and initial pH (2, 3, 4, 5, 6, and 7) on the removal efficiency and capacity of Cr(VI) by Mxene–CS composites were measured, respectively.

$$\text{Removal efficiency} = \frac{X_0 - X_e}{X_0} \times 100\% \quad (1)$$

$$q = \frac{(X_0 - X_e) \times V}{m} \quad (2)$$

where X_0 (mg/L) and X_e (mg/L) are presenting the original concentration and equilibrium concentration of Cr(VI) in the solution, respectively, V (L) is the volume of the potassium bichromate solution, and m (g) is the mass of Mxene–CS used in the batch experiment.

2.4.1. Adsorption Kinetic Model

The adsorption kinetic model was adopted to investigate the adsorption control mechanism of Cr(VI) by Mxene–CS [39]. The adsorption experiments were carried out in the

Cr(VI) solution (50 mg/L), then further fit the results by using pseudo-first-order kinetic model and pseudo-second-order model as described by Equations (3) and (4) [40,41].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e is adsorption capacity at equilibrium (mg/g), q_t is the sorption capacity at a certain reaction time (mg/g), t is the reaction time (min), k_1 is the first-order rate constant (min^{-1}), and k_2 is the second-order rate constant (g/mg min^{-1}).

2.4.2. Adsorption Isotherm

In addition to the adsorption rate, the adsorption capacity is also an important index for the adsorbent's large-scale application in the industry. The removal data of Cr(VI) by Mxene-CS were fitted by using two typical isothermal adsorption models (Langmuir and Freundlich) to analyze the experiment data as shown in Equations (5) and (6) [2].

$$\frac{X_e}{q_e} = \frac{X_e}{q_{\max}} + \frac{1}{q_{\max} b} \quad (5)$$

$$\ln q_e = \ln K + \frac{1}{n} \ln X_e \quad (6)$$

where X_e is presenting the equilibrium concentration of Cr(VI) in the solution (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), $q_{\max}$ is the maximum adsorption capacity of Mxene-CS (mg/g), and b is a constant related to the adsorption energy. In Equation (6), n and K are the Freundlich empirical constants relating to the adsorption strength and the sorption capacity of the adsorbent, respectively.

2.4.3. Adsorption Thermodynamics

The adsorption thermodynamics was explored to make clear whether the adsorption process is exothermic or endothermic, while the Gibbs free energy change, entropy change, and enthalpy change of the adsorption process are calculated according to the thermodynamic formula as followed Equations (7)–(9).

$$\Delta G^0 = -RT \ln K_c \quad (7)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

where R is the gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and K_c is the thermodynamic equilibrium constant. A linear fit is performed by plotting $\ln K$ versus $1/T$, and ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the fitted curve.

3. Results and Discussion

3.1. Characterization of the Synthesized Mxene-CS

The Mxene was firstly prepared through etching of Ti_3AlC_2 by HF solution, while the appearance and schematic diagram from Ti_3AlC_2 to Mxene are shown in Figure 1a. The size of the prepared Mxene particles would get smaller, indicating the structure for the original Ti_3AlC_2 was partly changed. The XRD patterns (Figure 1b) were illustrating that the characteristic peak at 2θ of 39° could not be observed, indicating that the Al atoms were successfully etched out [42].

Figure 1. The preparation of Mxene by etching of Ti_3AlC_2 : (a) The appearance and schematic diagram, (b) the comparison of XRD patterns between the Ti_3AlC_2 and Mxene.

The SEM images of original Ti_3AlC_2 , Mxene, CS, and prepared Mxene–CS were shown in Figure 2. The pristine CS has a relative rough surface and compact structure, while the Mxene (after treatment of Ti_3AlC_2 powders by HF solutions) had a smoother surface and a typical two-dimensional layered structure, indicating that the Mxene was successfully prepared from the Ti_3AlC_2 . For the Mxene–CS, the layered structure of Mxene does not completely disappear, and the irregular compact particles observed in the SEM image, indicating that CS was successfully loaded on the Mxene. The generation of the uneven surface and the pore structure in the Mxene–CS should enhance its specific surface area, which is beneficial to the contact between the surface-active group of Mxene–CS and the Cr(VI) pollutants in the aqueous solution. The XRD patterns and FT-IR spectra of Mxene, CS, and prepared Mxene–CS are shown in Figure 3. In the prepared Mxene–CS, the observed diffraction peaks observed at 2θ of 18.1° , 35.8° , 41.5° , and 60.1° were related to the Mxene. The rougher baseline for XRD of Mxene–CS also illustrated that the CS was entering into the Mxene. For the FT-IR spectra, the characteristic peaks of $-\text{NH}_2$ group (observed at 1635 and 1517 cm^{-1}) and $-\text{OH}$ group (at 3482 cm^{-1}) in the CS are also presented in the Mxene–CS, indicating that the CS has been successfully entered into the prepared composite.

Figure 2. SEM images of the original Ti_3AlC_2 (a), the Mxene (b), CS (c), and prepared Mxene–CS (d).

Figure 3. (a) XRD patterns of Mxene, CS, and prepared Mxene-CS. (b) FT-IR spectra of Mxene, CS, and prepared Mxene-CS.

3.2. Removal of Cr(VI) by Mxene-CS

3.2.1. Effect of Mxene-CS Dosage

The removal efficiency and capacity of Cr(VI) (50 mg/L) by the prepared Mxene-CS was shown in Figure 4. As shown, the removal efficiency of Cr(VI) was increased from 12.9% to 40.5% with Mxene-CS dosage ranging from 0.02 to 0.12 g/L, while the removal capacity was decreased from 30.5 to 16.1 mg/g. The progress of Cr(VI) removal efficiency was mainly attributed to more contact surface area and adsorption sites. However, the amount of Cr(VI) (which could be absorbed and removed) is limited, with more Mxene-CS in the aqueous solution, the amount of Cr(VI) adsorbed by per amount of Mxene-CS would be decreased as shown in Figure 4.

Figure 4. Effect of Mxene-CS dosage on the adsorption capacity and rate of Cr(VI) (Conditions: Adsorption temperature of 25 °C, pH of 4.3, and reaction time of 24 h).

3.2.2. Adsorption Kinetics Study

The adsorption kinetics results of Cr(VI) at varying initial Cr(VI) concentrations were shown in Figure 5, indicating that the removal efficiency increased within the initial 400 min and reached the equilibrium within 480 min at Mxene-CS dosage of 100 mg/L. The adsorption capacity (at equilibrium point) was calculated as 50.6, 13.0, and 10.10 mg/g at the initial Cr(VI) concentration of 100, 50, and 20 mg/L, respectively. It is obvious

that the adsorption capacity is increasing slower after 480 min for the adsorption capacity of Mxene-CS reached saturation. Thus, the optimum reaction time was determined as 480 min.

Figure 5. The adsorption capacity of Cr(VI) by Mxene-CS (0.6 g/L) with varying initial Cr(VI) concentration (Conditions: Adsorption temperature of 25 °C and pH of 4.3).

In order to further investigate the adsorption kinetics of Cr(VI) by Mxene-CS, the adsorption data were fitted with the pseudo-first-order kinetic model and the pseudo-second-order kinetic model (Table 1). The fitting kinetic curves were presented in Figure 6, while the higher R^2 value (0.9952) suggests that the removal of Cr(VI) by Mxene-CS is more prone to the pseudo-second-order kinetic model, further indicating that this removal process should be controlled by the chemical adsorption.

Table 1. The parameters for kinetic models of Cr(VI) removed by Mxene-CS.

Concentration (mg/L)	Pseudo-First-Order Model			Pseudo-Second-Order Model		
	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg·min)	R^2
100	15.62	0.0032	0.5942	53.48	0.0003	0.9952
50	24.03	0.0053	0.5975	22.54	0.0002	0.9633
20	12.91	0.0028	0.6899	14.60	0.0002	0.9530

Figure 6. Fitting model for the Cr(VI) adsorption: The pseudo-first-order model (a), and the pseudo-second-order model (b).

3.2.3. Adsorption Isotherm Study

To further evaluate the removal capacity of Cr(VI) on Mxene–CS, the adsorption isotherm of Cr(VI) at different experimental conditions was investigated and is shown in Figure 7, while the corresponding fitting parameters are shown in Table 2. The Langmuir isotherm (with R^2 value of 0.9693 at 298 K) was observed to better fit the adsorption behaviors of Cr(VI) by Mxene–CS, indicating that the adsorption process is mainly monolayer adsorption. This is also consistent with the chemisorption process proved by pseudo-second-order kinetic model from the adsorption kinetics study.

Figure 7. The Langmuir isotherm model curve for Mxene–CS (a–c) and the Freundlich isotherm model curve (d–f).

Table 2. The parameters and correlation coefficients for the Langmuir and Freundlich isotherm model.

T(K)	Langmuir Parameters			Freundlich Parameters		
	q_{max} (mg/g)	K_L (L/mg)	R^2	$1/n$	K_f	R^2
298	43.10	0.1305	0.9693	0.5205	$e^{1.6761}$	0.8576
308	43.48	0.2005	0.9659	0.4058	$e^{2.1217}$	0.9058
318	44.25	0.2545	0.9631	0.3794	$e^{2.2497}$	0.8910

3.2.4. Adsorption Thermodynamics Study

The adsorption thermodynamics of Cr(VI) by the prepared Mxene–CS were also studied and are shown in Figure 8 and Table 3. The adsorption free energy (ΔG^0) of negative values indicated that the adsorption of Cr(VI) by Mxene–CS is a spontaneous process. The enthalpy change value (ΔH^0) is more than zero, illustrating that the adsorption process is an endothermic reaction, which could explain the phenomenon that the adsorption efficiency of Cr(VI) was increased with increasing temperature. ΔS^0 is the algebraic sum of the entropy change of the reaction system, representing the degree of chaos. The adsorption entropy change (ΔS^0) is also more than zero, indicating that the obtained entropy (caused by desorption of water molecules) would exceed the entropy lost by the adsorption process.

Figure 8. Thermodynamic fitting curve of adsorption of Cr(VI) on Mxene-CS.

Table 3. Thermodynamic parameter values for Cr(VI) adsorption.

T	ΔG^0 (kJ/mol)	ΔS^0 (J/mol)	ΔH^0 (kJ/mol)
298	−0.2522	22.0146	81.3084
308	−0.3820		
318	−0.4177		

3.3. Effect of pH

As pH values are variable in the actual water environment, the adsorption rate of Cr(VI) by Mxene-CS at pH ranging from 2 to 7 was investigated and is shown in Figure 9a. As shown, the pH would affect the adsorption capacity of Cr(VI) by the Mxene-CS, with the maximum capacity of 22.3 mg/g at pH of 4. To study the effects on Mxene-CS, we measured the zeta potential of the composite at different pH. The effect of pH on the zeta potential of Mxene-CS is shown in Figure 9b. The surface charge of Mxene-CS is all positive at pH ranging from 2 to 10, with the maximum value at pH around 4–6. Thus, at pH 2–7, the Mxene-CS surface is positively charged and has an electrostatic attraction between the composite and the negatively charged $\text{Cr}_2\text{O}_7^{2-}$. The decrease of adsorption capacity at pH ranging from 4 to 7 reflects the reduction in the zeta potential [5].

Figure 9. Effect of solution pH on adsorption performance of Cr(VI): (a) The influence of pH on adsorption capacity (Conditions: Temperature of 25 °C, and reaction time of 24 h), (b) the Zeta potential of Mxene-CS in the aqueous solution.

The XPS spectra for chemical states of Ti, C, Cr, and O were measured before and after the adsorption process, as shown in Figure 10a. It was found that a Cr 2p peak was observed at near 577.4 eV after Cr(VI) adsorption, indicating adsorption of Cr(VI) has occurred [43]. The XPS spectra of the Cr 2p core level are shown in Figure 10b, while the Cr 2p_{1/2} and Cr 2p_{3/2} peaks near 586.68 eV and 577.4 eV were detected, indicating that Cr(VI) was contacted and removed to the surface of the composite [43]. The comparison for removal of Cr(VI) by different materials from an aqueous solution is shown in Table 4. Compared with the prepared Chitosan–FeO nanoparticles, nZVI–multiwalled carbon nanotube, ZVMg, and modified brown algae, Sargassum bevanom, the removal performance of Cr(VI) by the Mxene–CS in this study is partly restricted, probably attributed to the relatively weak combination between the Mxene and CS at the certain molar ratio [24]. To expand its practical application in the actual wastewater, varying molar ratios of Mxene to CS on synthesizing of the novel composite are recommendable.

Figure 10. XPS spectra from Mxene–CS before and after adsorption: (a) Full–range XPS spectra, (b) Cr 2p.

Table 4. Comparison for removal of Cr(VI) through different materials from an aqueous solution.

Order	Adsorbent	Optimum Condition (°C, pH, and the Dosage of Materials)	Initial Cr Concentration (mg/L)	Removal Efficiency (%)	Removal Capacity (mg/g)	Cited Reference
1	Chitosan–FeO nanoparticles	20, 6.0, 0.4 g/L	70	—	60.2 (the theoretical removal capacity)	[44]
2	nZVI–multiwalled carbon nanotube	30, 7.0, 0.1 g/L	20	98%	—	[45]
3	bentonite–supported nanoscale zero–valent iron	30, 5.0, 4 mg/L	20	99.8%	—	[46]
4	ZVMg	21, 7.0, 0.05 g/L	18.6	100%	—	[47]
5	ZVMg/combined with ultrasonic power treatment (100 W)	20–25, >7, (2.5 g/L, 5 g/L, and 10 g/L)	50	100%	—	[48]
6	ZVI/MgO	20, 5.0, 16 g/L	30	97%	—	[49]
7	Modified brown algae Sargassum bevanom	Room temperature, 3, 7 g/L	100	89.64%	—	[9]
8	Mxene–CS (This study)	25, 4.3, 0.6 g/L	100	30.4%	50.6 mg/g	This study

— presenting “not mentioned”.

4. Conclusions

In this study, the Mxene–CS composite was successfully prepared by the simple solution method and applied in the removal of Cr(VI) from the aqueous solution. The following conclusions can be drawn from the batch experiment.

(1) In the prepared Mxene–CS, the layered structure of Mxene does not completely disappear, with the irregular compact particles detected, indicating that CS was successfully loaded on the Mxene.

(2) The effects of parameters, including Mxene–CS dosage and pH, on the removal of Cr(VI) from the aqueous solution were investigated. With the Mxene–CS dosage ranging from 0.02 to 0.12 g/L, the removal efficiency of Cr(VI) was increased from 12.9% to 40.5%. The influence of pH on the removal of Cr(VI) by the Mxene–CS was mainly controlled by the varying potential at different pH.

(3) The removal of Cr(VI) by Mxene–CS is more prone to the pseudo-second-order kinetic model, indicating the removal process should be controlled by the chemical adsorption. The Langmuir isotherm was more suitable to describe the adsorption behaviors of Cr(VI) by Mxene–CS, with the maximum adsorption capacity of 43.1 mg/g.

This experiment should provide a reliable theoretical basis for Mxene–CS adsorption of Cr(VI), and further expand the application prospect of inorganic–organic composites in wastewater.

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