Alkali treated $Ti_3C_2T_x$ MXenes and their dye adsorption performance

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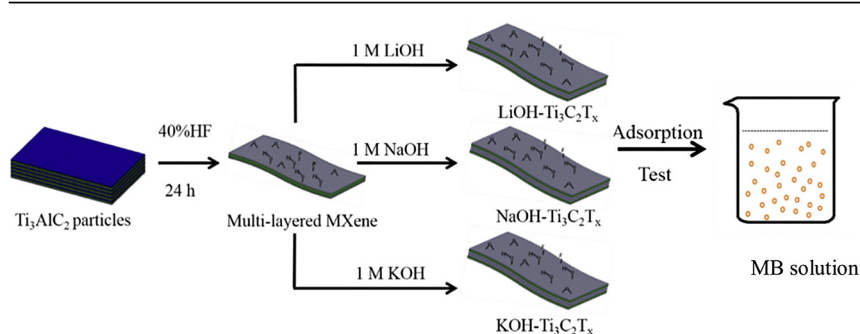
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HIGHLIGHTS

- The c-LC expansion of Alk- $Ti_3C_2T_x$ was ascribed to alkali metal ions intercalation.
- Adsorption mechanism for Alk- $Ti_3C_2T_x$ is revealed.
- The enhanced adsorption of Alk- $Ti_3C_2T_x$ can be described by a Langmuir isotherm.

GRAPHICAL ABSTRACT



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ABSTRACT

To modify the adsorption performance of $Ti_3C_2T_x$ MXene, we report a facile approach to expand the interlayer spacing of $Ti_3C_2T_x$ and to tune its surface functional groups by hot alkaline solution treatment. In the treatment, the interlayer spacing of $Ti_3C_2T_x$ MXene is increased by up to 29% by LiOH, and the surface functional groups are tuned by converting -F to -OH. Among the MXenes, LiOH- $Ti_3C_2T_x$ and NaOH- $Ti_3C_2T_x$ can faster adsorb methylene blue (MB) than other MXene adsorbents; NaOH- $Ti_3C_2T_x$ possesses the highest adsorption capacity (189 mg/g) for MB, which can be ascribed to the cooperation of surface adsorption and intercalation adsorption. The experimental data suggest that the enhanced adsorption toward cationic dyes can be best described by a Langmuir isotherm.

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1. Introduction

Water contamination caused by dyes has become a severe problem, since the discharge of dyes into water pollutes the environment and thus jeopardizes human health [1,2]. Various methods

including biological treatment, adsorption, chemical oxidation, membrane separation, electrodialysis and ion exchange have been developed for dye sewage treatment [3–9]. Among these methods, adsorption technology is an ideal approach to remove dyes in sewage discharge for its low cost and simplicity of operation [10]. A number of materials have been reported to remove dyes by adsorption, including activated carbon, montmorillonite clay, kaolinite, fly ash, polymer, etc. [11–15]. Meanwhile, new materials with high adsorption capacity and adsorption efficiencies are explored for dye pollution control [16].

Because of the large specific area and fast removal rate, two

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dimensional (2-D) materials are capable absorbents for environmental remediation via physical or/and chemical adsorption [17]. However, the application of traditional 2-D materials is limited by their features of single element (Graphene), weak bond (van der Waals bonding), low production efficiency and lack of surface functional groups, etc. [18].

Very recently, a newly emerging family of 2-D materials named MXenes have attracted attention due to their potential to overcome these drawbacks. MXenes are derived from their MAX precursor (short for $M_{n+1}AX_n$, where M is an early transition metal, A is group A element, X is carbon and/or nitrogen, and $n = 1, 2, \text{ or } 3$) by selectively extracting A atoms [19,20]. MXene can be denoted as $M_{n+1}X_nT_x$, where M and X remain from its precursor, and T_x represents surface termination groups ($-\text{OH}$, $-\text{F}$, $=\text{O}$) created in the etching process. The environment-friendly MXenes not only share the common merits of traditional 2-D materials, but also show superior characteristics, such as high electrical conductivity, hydrophilia, fine structure, chemical stabilities, etc. [21–27], which makes MXenes promising candidates for wastewater treatment and ion separation [28–30]. Mashtalir [31] firstly showed that pristine $\text{Ti}_3\text{C}_2\text{T}_x$, a representative of MXene family, is an efficient adsorbent for the cationic dye MB. Peng [18] found that NaOH treated $\text{Ti}_3\text{C}_2\text{T}_x$ exhibit unique adsorption behavior for toxic Pb(II). Ying [32] demonstrated that exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets can remove Cr(VI) rapidly and effectively. However, the dye adsorption behavior of alkali treated MXenes has not been reported, and their adsorption mechanism is unclear yet. In this work, the comparative study of MB adsorption performance of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and alkali treated $\text{Ti}_3\text{C}_2\text{T}_x$ (Alk- $\text{Ti}_3\text{C}_2\text{T}_x$) was conducted, and the adsorption mechanism for Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ is revealed.

2. Materials and methods

2.1. Materials preparation

Synthesis of Ti_3AlC_2 : Starting powders of TiC ($2\text{--}4\ \mu\text{m}$), Al ($<48\ \mu\text{m}$) and Ti ($<48\ \mu\text{m}$) in a 1.8:1:1 M ratio were mixed in a Turbula mixer for 24 h. The mixtures were heated in an electric tube furnace in an argon flow (40 mL/min). The furnace was heated to $1000\ ^\circ\text{C}$ at $10\ ^\circ\text{C}/\text{min}$, and then to $1450\ ^\circ\text{C}$ at $5\ ^\circ\text{C}/\text{min}$, and after soaking at $1450\ ^\circ\text{C}$ for 2 h, the furnace was cooled down.

The resulted brick was ground with an agate mortar and sieved through a 300-mesh sieve, obtaining Ti_3AlC_2 powders with particle size less than $48\ \mu\text{m}$.

Synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene: $\text{Ti}_3\text{C}_2\text{T}_x$ was fabricated according to reference [19]. Typically, 3 g of as-prepared Ti_3AlC_2 powders were added into 60 mL of 40 wt% hydrofluoric acid (HF, Aladdin Industrial Corporation) solution at 298 K, and then the system had reacted for 24 h under magnetic stirring. The resultant was then washed through distilled water addition, centrifugation (4000 rpm, 3–5 min for each cycle), and decanting, until the supernatant reached a pH of approximate 6. The final product was dried in a vacuum oven at $50\ ^\circ\text{C}$ for 24 h.

Synthesis of Alk- $\text{Ti}_3\text{C}_2\text{T}_x$: LiOH- $\text{Ti}_3\text{C}_2\text{T}_x$ was synthesized by soaking 1 g of $\text{Ti}_3\text{C}_2\text{T}_x$ in 100 mL of 1 mol LiOH aqueous solution at $80\ ^\circ\text{C}$ under magnetic stirring for 1 h. After filtration and washing with distilled water (the supernatant reached a pH of approximate 8), the LiOH treated powder was dried in a vacuum oven at $60\ ^\circ\text{C}$ for 12 h. NaOH- $\text{Ti}_3\text{C}_2\text{T}_x$ and KOH- $\text{Ti}_3\text{C}_2\text{T}_x$ were synthesized by the same procedure by simply replacing the LiOH aqueous solution with NaOH or KOH solution.

2.2. Characterization

The phase constitutions of samples were characterized by X-ray

diffraction (XRD) (SmartLab (3)) with Cu K α under 40 kV and 30 mA. A step interval of 0.02° and scanning speed of $10^\circ/\text{min}$ were used. The microstructural morphology of samples was observed by field emission scanning electron microscopy (FESEM) (Sirion 200, FEI) equipped with EDS (Pegasus 2040, EDAX) and transmission electron microscopy (TEM) (Tecnai G2 20, FEI Company, USA).

2.3. Evaluation of dye adsorption performance

Absorption performance of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ was examined by measuring the absorption rate of MB (AR, Tianjin Fuchen Chemical Reagents Factory) in an aqueous solution. 100 mg of adsorbent of Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ and 200 mL of 50 mg/L MB aqueous solution were added into a flask in dark environment ($\text{pH} = 7\text{--}7.2$, RT). The flask was installed in a shaker (150 r/min, $25\ ^\circ\text{C}$), and after every 20 min, 5 mL solution was extracted and centrifuged to obtain supernate. Thereafter the supernate was tested to measure the maximum absorbance by UV–vis spectrometry (Varian Cary 5000) and evaluate the residual concentration of MB. The concentration of residual MB was calculated by comparing the absorption peak of MB at 664 nm. The MB adsorption performance of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ MB was evaluated by the MB removal rate, and it was calculated by the following equation (1):

$$\text{Removal}(\%) = \frac{(C_0 - C_r)}{C_0} \times 100 \quad (1)$$

Where C_0 (mg/L) and C_r (mg/L) are the initial and residual concentrations of MB in aqueous solution, respectively.

The adsorption isotherm of Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ was conducted by adding an amount of Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ into a series of MB aqueous solution at natural pH and shaking for 24 h in the dark to allow it to reach equilibrium. The MB adsorption capacity (Q) of Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ was calculated by the following equation (2):

$$Q = \frac{(C_0 - C_r)}{m} V \quad (2)$$

Where Q (mg/g) is the MB removal capacity. V (L) is the volume of aqueous solution and m (g) is the weight of $\text{Ti}_3\text{C}_2\text{T}_x$ or Alk- $\text{Ti}_3\text{C}_2\text{T}_x$.

3. Results and discussion

3.1. Structure and composition

Fig. 1 displays the XRD pattern of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ with broad peaks and low intensity, indicating the disorder of crystal structure caused by the extraction of Al out of the parent Ti_3AlC_2 . After alkaline treatment (LiOH, NaOH and KOH), the characteristic peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ become clearer and stronger (Fig. 1II–1IV), with the (002) peak shifted to lower angle considerably, implying that ions intercalation not only swells the structure of the $\text{Ti}_3\text{C}_2\text{T}_x$ but also increases the homogeneity of the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets, especially for NaOH- $\text{Ti}_3\text{C}_2\text{T}_x$ and KOH- $\text{Ti}_3\text{C}_2\text{T}_x$. The distinct shift of the (002) peaks for Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ to lower angle reveals that alkali metal ions (Li^+ , Na^+ and K^+) intercalated into MXene layers, which led to considerable increment on c -LC (lattice constant) ($4.48\text{--}5.96\ \text{\AA}$). The trapped Li^+ , Na^+ and K^+ cations, served as pillars, as well as the penetrated solvent molecules and the repulsion force between surface functional groups, cooperated to expand and swell the interlayer distance. This phenomenon is an intrinsic property for layer structure materials, such as graphite [33], kaolinite [34].

The c -LC of MXene equals to 2d spacing of [002] planes [35]. The results derived from the XRD patterns according to Bragg's law are shown in Table 1. It is evident that the c -LC for Alk- $\text{Ti}_3\text{C}_2\text{T}_x$ decrease

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