Magnetic Ti$_3$C$_2$ MXene Nanomaterials for Doxorubicin Adsorption from Aqueous Solutions: Kinetic, Isotherms, and Thermodynamic Studies

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ABSTRACT: In this work, the magnetic Ti$_3$C$_2$ MXene functionalized with β-cyclodextrin was prepared and characterized using scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectra, X-ray diffraction, X-ray photoelectron spectroscopy, vibrating sample magnetometry, and thermogravimetric analysis. The synthesized nanomaterial was used as an adsorbent to adsorb doxorubicin from aqueous solutions, and the experimental parameters that affected the adsorption efficiency were investigated. In addition, the adsorption characteristics including adsorption kinetics, adsorption isotherm, and thermodynamics were researched comprehensively. The adsorption kinetics of doxorubicin followed a pseudo-second-order kinetic model, which indicated that adsorption was the rate-limiting step, and the maximum adsorption capacity was 7.35 μg mg$^{-1}$ by shaking for 60 min at pH 7.0. The adsorption isotherm was well described using the Freundlich model, which implied that multilayer adsorption took place over the prepared nanomaterial for doxorubicin adsorption. The negative values of Gibbs free energy change ($\Delta G^0 < 0$) demonstrated that doxorubicin adsorption was a spontaneous process. The positive values of entropy change ($\Delta S^0 > 0$) implied that doxorubicin adsorption was an increasing random process. Enthalpy change values were positive ($\Delta H^0 > 0$) and indicated that the adsorption of doxorubicin was endothermic. The adsorption percentage of doxorubicin remained ~99.7% for ciprofloxacin from wastewater, which revealed that MXenes can be used as a novel adsorption nanomaterial with great potential in environmental applications.

1. INTRODUCTION

In recent years, two-dimensional (2D) structure materials have shown unique physical and chemical properties compared with other materials. MXene (e.g., Ti$_3$C$_2$T$_x$), a family of 2D materials, has attracted wide interest since its discovery in 2011 because of its relatively large specific surface area, high electrical conductivity, and hydrophilicity. The general formula of MXene is often described as $\text{M}_{n+1}\text{X}_n\text{T}_x$ (M, X, and T$_x$ represent a transition metal, carbon/nitrogen, and surface functional groups such as $-\text{OH}$, $-\text{O}$, and $-\text{F}$), and they are produced by selective etching of IIIA or IVA elements from the MAX phase (e.g., Ti$_3$AlC$_2$). MXene has shown huge potential in multiple fields, such as sensors, energy storage, cancer therapy, and EM wave absorption and shielding. Because of the large specific surface area, hydrophilic performance, tunable surface chemistry, high negative zeta potential, and environment-friendly characteristics, MXene has attracted wide attention in adsorption and remediation of wastewater. For example, Ti$_3$C$_2$ MXene exhibited a high adsorption efficiency with the removal rate enhanced up to ~99.7% for ciprofloxacin from wastewater, which revealed that MXenes can be used as a novel adsorption nanomaterial with great potential in environmental applications.

Doxorubicin (DOX) is an effective anticancer drug, which can significantly inhibit the growth of tumor cells. However, it will lead to a variety of adverse side effects and multidrug resistance effects in cancer treatments because it cannot distinguish between normal cells and tumor cells. Eventually, after administration to patients, it may be released into the environment through excretions as mixtures of its original form and their metabolites. The detection of DOX in oncologic hospital wastewater in some areas was in the range of 0.26–1.35 μg L$^{-1}$, and 0.02–0.042 μg L$^{-1}$ was detected in hospital wastewater.
wastewater treatment plants.\textsuperscript{12} Eco-genotoxicity studies revealed that DOX causes DNA damage to Ceriodaphnia dubia cells at a concentration of 0.05 \( \mu \text{g L}^{-1} \). Thus, DOX has been one of the contaminants in the list of emerging substances because of the potential risks.\textsuperscript{13} The solubility of DOX is extremely low in neutral water and could pose harmful effects on growing eukaryotic organisms because of its toxicity, genotoxicity, mutagenicity, and teratogenicity.\textsuperscript{14} Various treatment methods such as membrane technology, activated carbon, exchange resins method, and advanced oxidation technology have been tried for the elimination of pharmaceutical residues from water.\textsuperscript{13,15,16} Unfortunately, secondary pollutants may be formed in aqueous solutions because of the complex structures and variable physicochemical properties of DOX.\textsuperscript{17,18} Accordingly, it is necessary to find a more effective method for removing DOX.

Adsorption technology is considered to be a promising method for removing pollutants from effluents.\textsuperscript{19} Some kinds of absorbents such as carbon nitride, carbon nanotubes, and graphene nanoribbons have been used for adsorption of DOX from aqueous solutions,\textsuperscript{19,20,21} but some shortcomings such as time consumption and difficult separation exist.\textsuperscript{22} Recently, iron oxide nanoparticles (Fe\(_3\)O\(_4\) NPs) have attracted extensive attention in the field of environmental remediation.\textsuperscript{23,24} However, unmodified Fe\(_3\)O\(_4\) NPs are difficult to recycle in practical application because they are easy to agglomerate and form clusters.\textsuperscript{25} Up to now, various magnetic adsorbents that were modified or coated different groups on the surface of Fe\(_3\)O\(_4\) NPs to provide functionality and stability have been prepared for inorganic, organic, and biological analysis.\textsuperscript{26,27} For example, multilayer cucurbit[6]uril-based magnetic nanoparticles were prepared based on host-guest interactions by Jia’s group, and the compound was successfully used as a blood purification material to remove lipoprotein from plasma.\textsuperscript{28}

\( \beta \)-cyclodextrin (\( \beta \)-CD) is a kind of nontoxic cyclic oligosaccharides, and the most significant structure is hydrophilic exterior and hydrophobic interior cavity.\textsuperscript{29,30} It is well known that \( \beta \)-CD can form stable host-guest inclusion complex with a variety of aromatic molecules into its hydrophobic cavity though host-guest interactions.\textsuperscript{30} However, the inherent solubility of \( \beta \)-CD hinders its practical application in a variety of areas.\textsuperscript{30} \( \beta \)-CD has many reactive hydroxyl groups with high chemical reactivity, which offer abundant active centers for the reaction with organic functional groups, making it possible for new functionalization.\textsuperscript{31} Furthermore, chemical modification can be conducted at the upper and lower edges to improve solubility and inclusion efficiency and further to construct various functional materials.\textsuperscript{12}

In this study, magnetic Ti\(_3\)C\(_2\) MXene functionalized with \( \beta \)-CD was prepared (Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@\( \beta \)-CD) and used as an adsorbent for adsorption of DOX from aqueous solutions. The experimental parameters that affected the adsorption efficiency were investigated, and the experimental data were analyzed based on adsorption kinetics, adsorption isotherm models, and thermodynamics. After that, the performance of interference and regeneration was also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Ti\(_3\)AlC\(_2\), \( \beta \)-cyclodextrin (\( \beta \)-CD), hydrofluoric acid (HF), doxorubicin (DOX), allyl bromide, p-toluenesulfonfonyl chloride (TsCl), ethylene glycol, dimethylsulfoxide (DMSO), ferric chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), ammonium hydroxide (NH\(_4\)\(_2\)H\(_2\)O, 25%, w/w), (3-mercaptopropyl) triethoxysilane (MPTMS), and polyethylene glycol (PEG-2000, \( M_w \) = 2000) were obtained from Macklin Reagent (Shanghai, China). Acetic acid, sodium chloride (NaCl), hydrochloric acid (HCl), sodium acetate, sodium hydroxide (NaOH), phosphoric acid (H\(_3\)PO\(_4\)), nitric acid (HNO\(_3\)), sodium hydrogen phosphate (Na\(_2\)HPO\(_4\)), sodium dihydrogen phosphate (NaH\(_2\)PO\(_4\)), and ethanol were purchased from Jiangsu Qiangsheng Chemical Co., Ltd. (Changshu, China). The DOX stock solution (100 \( \mu \text{g mL}^{-1} \)) was prepared by deionized water. The grade of NdFeB strong magnet is N35, and the residual magnetic flux density is 11,700–12,200 Gs.

2.2. Methodology. The synthesized magnetic nanoparticles were characterized using scanning electron microscopy (SEM, S-4800, JEOL Company, Japan; QUANTA-250, Thermo, USA), transmission electron microscopy (TEM, H-7800, Hitachi, Japan), Fourier transform infrared (FT-IR, Bruker), vibrating sample magnetometry (VSM, MMPS SQUID XL-7, Quantum Design, USA), and thermogravimetric analysis (TGA, STA2500, Netzsch, Germany). In addition, the concentration of DOX was determined by measuring the absorbance using a UV–visible spectrophotometer (CARY100, Agilent, USA) at a wavelength of 483 nm.

2.3. Preparation of Ti\(_3\)C\(_2\) MXene Nanosheets. Ti\(_3\)AlC\(_2\) (1.0 g) was slowly added in HF (10 mL) to stir for 48 h at 50 °C for complete removal of the Al layers. Then, the solution was centrifuged and rinsed several times with deionized water to remove the unreacted HF until pH > 6.0. Then, the obtained Ti\(_3\)C\(_2\) powder was vacuum-dried at 40 °C.

2.4. Preparation of Fe\(_3\)O\(_4\) NPs. Fe\(_3\)O\(_4\) NPs were prepared according to our previous work.\textsuperscript{33} FeCl\(_3\)·6H\(_2\)O (2.7 g) was added to a flask and dissolved with ethylene glycol (50 mL). After stirring violently for 30 min, the color of the solution changed from colorless to orange. Then PEG-2000 (2.0 g) and sodium acetate (7.2 g) were added to the solution and stirred for 1 h. The brown sticky solution was transferred into a Teflon-lined stainless-steel autoclave and sealed, and the autoclave was heated to 200 °C for 9 h. After that, the obtained black precipitate was washed several times with ethanol and deionized water until neutral and was dried at an ambient temperature in vacuum.

2.5. Preparation of Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@\( \beta \)-CD. Ti\(_3\)C\(_2\) MXene (100 mg) and Fe\(_3\)O\(_4\) NPs (50 mg) were dispersed in 80 and 20 mL of deionized water, respectively, and allowed to stir for 30 min. Then, the above solution was mixed and ultrasound-treated for 120 min under N\(_2\). After that, the resulting black precipitate was collected using an NdFeB strong magnet and washed several times with ethanol and deionized water. Finally, Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\) was obtained and dried at 50 °C overnight.

Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@MPTMS was obtained with the surface of Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\) modified via the grafting of MPTMS as an organosilane. Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\) (0.1 g) was dispersed into the solution of DMSO/MPTMS (v/v, 80:2), and the mixture was stirred for 5 h at 80 °C to obtain Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@MPTMS.

Allyl-\( \beta \)-CD was synthesized according to Zhang’s work.\textsuperscript{34} Then, Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@\( \beta \)-CD magnetic nanomaterials were prepared by thiol-ene click reaction between —SH of MPTMS and C=C of allyl-\( \beta \)-CD. Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@MPTMS, and AIBN (1 wt %) was added to the DMSO, and the mixture was allowed to stir for 4 h at 75 °C. The obtained Ti\(_3\)C\(_2\)@Fe\(_3\)O\(_4\)@\( \beta \)-CD magnetic nanomaterials
were separated using an NdFeB strong magnet and then washed with ethanol and deionized water several times. The obtained products were dried under vacuum at 60 °C overnight. The synthesis process of Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was illustrated in Figure 1.

Figure 1. Synthesis of Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD.

2.6. Adsorption Experiments. The DOX adsorption process onto the Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was conducted as follows: Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD (5 mg) was mixed with DOX solution (15 mL, 5 μg mL$^{-1}$), and then, the mixture was mechanically shaken for 60 min at 25 °C. The DOX-adsorbed Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was separated using an NdFeB strong magnet. To evaluate the amount of adsorbed DOX, the adsorption percentage was measured using a UV–visible spectrophotometer at 483 nm.

The adsorption percentage of DOX was calculated according to the eq 1.

\[
\text{Adsorption (\%) = } \frac{C_0 - C_e}{C_0} \times 100\%
\]

where $C_0$ and $C_e$ are the equilibrium concentrations and initial concentrations (μg mL$^{-1}$), respectively.

In order to research and construct the adsorption isotherm of DOX onto the Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD, a series of concentrations of 2, 4, 6, 8, 10, 20, 30, 50, 80, and 100 μg mL$^{-1}$ DOX standard solutions (pH 7.0) were prepared and individually mixed with Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD (5 mg). The mixture was mechanically shaken for 60 min at 25 °C, and the adsorption capacity ($Q_e$) at equilibrium for DOX onto the Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was calculated as eq 2:

\[
Q_e = \frac{(C_0 - C_e) \times V}{m}
\]

where $Q_e$ is the adsorption capacity at equilibrium (μg mg$^{-1}$), $V$ is the volume of solution in (mL), and $m$ is the mass of the adsorbent (mg).

The kinetic study based on the DOX adsorption onto the Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was studied at different periods of time: 5, 10, 20, 30, 60, 90, 120, and 180 min, under the same batch conditions using 5 μg mL$^{-1}$ DOX (pH 7.0) and individually mixed with Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD (5 mg).

2.7. Desorption Experiments. Desorption experiments of DOX from Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was monitored that DOX-adsorbed Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was dispersed in ~5 mL of phosphate buffer solution (PBS) with pH 9.0. The experiment was carried out in an orbital shaker and maintained at 160 rpm for 30 min. Then, the supernatant was completely separated from the mixture solution using an NdFeB strong magnet for data analysis by UV–visible spectrophotometer at 483 nm.

2.8. Characterization. The morphologies of Ti$_3$C$_2$ and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD were obtained by SEM and TEM and are presented in Figure 2. Figure 2a, b illustrates the typical Ti$_3$C$_2$ MXene with the layered structure. After being etched, the tightly packed layers are obviously separated from each other and transformed into a loose accordion-like structure with a significant layer spacing because of the loss of Al atoms. After the incorporation of Fe$_3$O$_4$, a large number of regular spherical particles were immobilized uniformly into the structure of MXene nanosheets. Because of the thiol-ene click reaction between –SH of MPTMS and C=O of allyl-β-CD, the surface roughness of Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD was increased (Figure 2c, d).

The groups and structure of Ti$_3$C$_2$, Ti$_3$C$_2$@Fe$_3$O$_4$, and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD were characterized by FT-IR analysis. As shown in Figure 3, the strong peaks of 3440, 1100, and 598 cm$^{-1}$ were measured in Ti$_3$C$_2$@Fe$_3$O$_4$ and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD, which should be from the stretching vibration of O–H, C–F, and Fe–O–Fe, respectively. The O–H stretching vibration peak at 3440 cm$^{-1}$ exhibited a typical large red-shift relative to that of free O–H mode. Accordingly, it is reasonable to suppose that β-CD coexisted in the magnetic nanomaterial. In particular, the vibration of the Ti–O bond may account for the peak at 663 cm$^{-1}$.

Thus, the Ti$_3$C$_2$, Ti$_3$C$_2$@Fe$_3$O$_4$, and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD have been successfully synthesized.

The crystal structures of Ti$_3$C$_2$, Ti$_3$C$_2$@Fe$_3$O$_4$, and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD were investigated by XRD. As depicted in Figure 4, Fe$_3$O$_4$, Ti$_3$C$_2$@Fe$_3$O$_4$, and Ti$_3$C$_2$@Fe$_3$O$_4$@β-CD show similar diffraction patterns. Six characteristic peaks (2θ = 30.09, 35.47, 43.11, 53.61, 56.95, and 62.63°) were indexed to (220), (311), (400), (422), (511), and (440), respectively.
respectively, which match the face center cubic phase of Fe₃O₄ (JCPDS Card No. 19-629). There are a set of characteristic peaks at 2θ = 19.11, 33.96, 38.74, 41.76, and 60.18°, which corresponded to the (004), (101), (104), (105), and (109) planes of the Ti₃AlC₂ MAX phase. Three peaks in the Ti₃C₂ MXene XRD pattern at 2θ = 18.27, 33.96, and 60.18° were observed. However, the peak at 38.74° (104) disappeared completely in the XRD pattern of the obtained Ti₃C₂ MXene nanosheets, which revealed that the aluminum phase in Ti₃AlC₂ MAX was exfoliated during the etching process. Thus, the nanosheet structure of Ti₃C₂ MXene was successfully formed. Moreover, the (004) peak of the Ti₃C₂ MXene shifted toward the low-angle direction, which suggested the expansion of the MXene interlayer distance. The characteristic diffraction peaks at 18.27, 33.96, and 60.18° in Ti₃C₂@Fe₃O₄ and Ti₃C₂@Fe₃O₄@β-CD were attributed to the crystal planes (004), (101), and (109) of Ti₃C₂ MXene, respectively. The above results further demonstrated that Ti₃C₂@Fe₃O₄@β-CD maintain the primary structure of Ti₃C₂ MXenes.

Figure 5a demonstrated the survey XPS spectrum of Ti₃C₂ and Ti₃C₂@Fe₃O₄@β-CD, which mainly contained five elements corresponding to C, Ti, O, F, and Fe elements. The high-resolution XPS spectra of C 1s (Figure 5b) could be decomposed into four components. The peaks at 288.5, 286.3, 284.8, and 281.5 eV might be assigned as C=O, C–O, C–C, and C–Ti, respectively. The XPS spectra of O 1s are presented in Figure 5c. The peaks at 532.7, 531.0, and 530.0 eV were ascribed to the Ti–O, C=O, and C–O group, respectively. The Ti 2p spectra of Ti₃C₂@Fe₃O₄@β-CD (Figure 5d) were also studied. Four functional groups appeared at 464.6, 459.5, 458.3, and 454.9 eV, which were associated with Ti–O– Ti=O 2p1/2, Ti–O 2p3/2, and Ti–C, respectively. In addition, the relative elemental compositions of Ti₃C₂ and Ti₃C₂@Fe₃O₄@β-CD are summarized in Table 1. The relative content of Fe 2p and O 1s increased obviously compared with Ti₃C₂ but Ti 2p decreased. The results further indicated that Ti₃C₂@Fe₃O₄@β-CD was successfully synthesized.

Figure 6 illustrates the magnetization curves of Fe₃O₄, Ti₃C₂@Fe₃O₄, and Ti₃C₂@Fe₃O₄@β-CD, and the saturation magnetization values were calculated to be about 82.61, 35.57, and 29.48 emu g⁻¹, respectively. The results demonstrated that three samples have magnetic properties and they can be readily separated from the reaction media. The saturation magnetization of the Ti₃C₂@Fe₃O₄@β-CD was lower than that of two others, mainly due to the introduction of Ti₃C₂ and β-CD.

Figure 7 shows the weight losses of Ti₃C₂@Fe₃O₄@β-CD upon heating under air atmosphere from 10 to 1000 °C. Under the low temperature, it may be caused by the evaporation of free water adsorbed on the surface of Ti₃C₂@Fe₃O₄@β-CD nanomaterials. Under the high temperature, it may be caused by the functional groups of Ti₃C₂@Fe₃O₄@β-CD. The less weight loss indicated that Ti₃C₂@Fe₃O₄@β-CD showed remarked thermogravimetric stability.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optimization of Adsorption Conditions

Figure 8a depicts that the adsorption percentage of DOX onto the Ti₃C₂@Fe₃O₄@β-CD varies with the sample pH. The adsorption percentage increased from 10.79 to 34.87% when the pH enhanced from 2.0 to 7.0. The reason may be that the Ti₃C₂@Fe₃O₄@β-CD surface was positively charged when...
sample pH was low (pH_{pzc} is about 6.5); meanwhile, the electrostatic repulsion existed between DOX and TiC@FeO_{4}@β-CD surface.\textsuperscript{9} Besides, a competition between H\textsuperscript{+} ions and positively charged DOX molecules existing in the solution was presented on the surface of TiC@FeO_{4}@β-CD.\textsuperscript{14} With increased pH, the electrostatic repulsion will decrease. The molecular structure of DOX contains \(-\text{OH}\) and \(-\text{NH}_2\) groups, which can form hydrogen bonds with C=O and \(-\text{OH}\) groups on the surface of TiC@FeO_{4}@β-CD. The hydrogen-bonding interaction formed under natural conditions is stronger than that formed under acidic conditions. Regarding the structure and color alteration of DOX at the pH above 8.5, the adsorption percentage decreased obviously.\textsuperscript{17} Thus, pH 7.0 was chosen in further experiments.

The influence of adsorption time was evaluated in the range of 5–180 min, as shown in Figure 8b. The adsorption percentage can be obtained as 41% within 60 min and then increased by only 7% from 60 to 180 min, which indicated that longer adsorption time is of little significance for increasing the adsorption percentage. Thus, 60 min was adopted as the adsorption time for subsequent analysis.

Figure 8c describes the effect of different initial concentrations of DOX on the adsorption percentage. The results indicated that the adsorption percentage of DOX onto the TiC@FeO_{4}@β-CD increased observably when the initial concentration was increased from 2 to 15 \(\mu g\) mL\(^{-1}\), but it increased slowly later.

### 3.2. Adsorption Kinetics

Adsorption kinetics experiments help understand the dynamics and mechanism of the adsorption process. The kinetic study of DOX is also essential for designing and modeling the adsorption process by selecting optimal parameter conditions. In order to study the adsorption kinetics of DOX on adsorbents, the experimental data were analyzed by pseudo-first-order and pseudo-second-order kinetics models.\textsuperscript{45–47} The linear relationships are formed according to eqs 3 and 4,

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) are the amounts of DOX adsorbed at equilibrium and at time \(t\) (\(\mu g\) mg\(^{-1}\)), respectively. \(k_1\) and \(k_2\) are the rate constant of the pseudo-first-order models (min\(^{-1}\)) and the pseudo-second-order models (mg \(\mu g^{-1}\) min\(^{-1}\)), respectively.\textsuperscript{28,30}

The kinetic parameters for DOX adsorption onto the TiC@FeO_{4}@β-CD are illustrated in Table 2. The correlation factors for the pseudo-first-order kinetic plot was less than 0.99, whereas the pseudo-second-order kinetic plot exhibited correlation factors of 0.9960 for DOX adsorption. Pseudo-second-order rate constants \(q_e\) and \(k^2\) were calculated to be 7.35 \(\mu g\) mg\(^{-1}\) and 0.0144 mg \(\mu g^{-1}\) min\(^{-1}\) under experimental conditions, which could be determined from the slope and intercept of the line. The fitted value of \(q_e\) was very close to the experimental value of \(q_e\) (7.12 \(\mu g\) mg\(^{-1}\)), which further verified that DOX adsorption onto the TiC@FeO_{4}@β-CD are of the pseudo-second-order model. This implied that DOX adsorption could be dominated by chemisorption rather than physical adsorption. Chemisorption could be a result of host–guest interactions between DOX and β-CD or hydrogen-bonding interactions between TiC@FeO_{4}@β-CD and DOX.

### 3.3. Adsorption Isotherms

Adsorption isotherms provide valuable information about adsorption behavior, surface properties, and affinity of DOX toward the adsorbent. The amount of DOX-adsorbed on the TiC@FeO_{4}@β-CD surface and the amount of DOX remaining in the solution at a fixed temperature and pH at equilibrium can be evaluated by isotherms. The equilibrium adsorption of the TiC@FeO_{4}@β-CD was analyzed using Langmuir and Freundlich adsorption isotherms.\textsuperscript{35}

The Langmuir isotherm assumes monolayer adsorption on the homogeneous surface, where the adsorbed each adsorbate species has equal adsorption activation energy. The expression for the Langmuir isotherm is as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}
\]

Figure 8. Effect of (a) pH; (b) adsorption time; and (c) initial concentration.
Table 2. Kinetic Parameters for the Adsorption of DOX onto the Ti₃C₂@Fe₃O₄@β-CD

| qₑₑₑₑ (µg mg⁻¹) | k₁ (min⁻¹) | qₑₑₑₑ (µg mg⁻¹) | R² |
|------------------|------------|------------------|----|
| 7.12             | 0.0018     | 15.95            | 0.9010 |
|                  |            |                  |     |
|                  | 0.0144     | 7.35             | 0.9960 |

Table 3. Parameters of the Langmuir and Freundlich Isotherms for DOX Adsorption

| Langmuir model | Freundlich model |
|----------------|------------------|
| qₑₑₑₑ (µg mg⁻¹) | b (mL µg⁻¹) | R² | R_L | 1/n | K | R² |
| −90.09         | −0.035       | 0.4934 | −0.400−1.075 | 1.1424 | 2.194 | 0.9916 |

where Cₑ represents the equilibrium concentration of DOX in the supernatant (µg mL⁻¹); qₑ is DOX uptake at the adsorption equilibrium per weight of the adsorbent (µg mg⁻¹); qₑₑₑₑ is the maximum DOX adsorption capacity per weight of the adsorbent (µg mg⁻¹); and b is the Langmuir adsorption constant (mL µg⁻¹). The slope and intercept of the linear plot of Cₑ/qₑ against Cₑ yield the values of qₑₑₑₑ and b.

Also, the Langmuir isotherm can be employed to predict whether or not an adsorption process is favorable by a dimensionless constant separation factor, R_L, which is represented as follows:

\[ R_L = \frac{1}{1 + bC_0} \]  

where C₀ is the initial concentration of DOX (µg mL⁻¹). The value of R_L indicates that the shape of the isotherm and is defined as follows: R_L = 0 (irreversible), 0 < R_L < 1 (favorable), and R_L = 1 (linear).

The Freundlich isotherm is considered as model multilayer adsorption, which occurs on a heterogeneous surface, and its linear form can be expressed as follows:

\[ \log(q_e) = \frac{1}{n} \log(C_e) + \log k \]  

where k is the Freundlich constant indicative of adsorption capacity; 1/n is an empirical parameter that represents the adsorption capacity of the adsorbent and the energy of adsorption. k and n can be obtained from the intercept and the slope of the linear plot of log(qₑ) versus log(Cₑ), respectively. For the favorable adsorption process, the value of n should lie in the range of 1−10.

In this study, Langmuir and Freundlich isotherm models were fitted with experimental data, and then, the constants and correlation factors were calculated and listed in Table 3. Based on the correlation factor (R²) values, it can be deduced that the adsorption process of DOX onto the Ti₃C₂@Fe₃O₄@β-CD followed the Freundlich isotherm model owing to a high correlation value of 0.9916. This implied that multilayer adsorption took place over the Ti₃C₂@Fe₃O₄@β-CD. The assumption for this isotherm is that the interaction between the adsorbent surface and adsorbed molecules occurs on a heterogeneous surface, and the energy is distributed non-uniformly. The Langmuir isotherm model did not correlate with the experimental data. The plot of Cₑ/qₑ versus Cₑ does not follow a linear relationship, presenting a bad correlation coefficient (R² = 0.4934). It is apparent that the Langmuir model was unsuitable to describe the adsorption behaviors of DOX onto the Ti₃C₂@Fe₃O₄@β-CD.

3.4. Thermodynamic Studies. The adsorption behaviors of Ti₃C₂@Fe₃O₄@β-CD for DOX were critically investigated at 298, 308, and 318 K. Thermodynamic parameters are calculated from eqs 8, 9, and 10:

\[ \Delta G^0 = -RT \ln K_d \]  

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

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

where K_d is the distribution coefficient; R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹); and T is the temperature (K). Gibbs free energy change (ΔG⁰) was calculated using ln K_d values for different temperatures. Enthalpy change (ΔH⁰) and entropy change (ΔS⁰) are calculated from the slopes and intercepts of eq 10.

According to eq 10, the thermodynamic parameters were summarized in Table 4. The value of ΔH⁰ confirmed that the DOX adsorption progress onto the Ti₃C₂@Fe₃O₄@β-CD was endothermic and the adsorption percentage of DOX increased with temperature. The value of ΔS⁰ indicated a greater order of reaction during DOX adsorption and the negative values of ΔG⁰ reflected the DOX adsorption progress onto the Ti₃C₂@Fe₃O₄@β-CD was a spontaneous and feasible process.

3.5. Desorption and Regeneration. To investigate the possibility of Ti₃C₂@Fe₃O₄@β-CD regeneration, the desorption experiments were performed. The results showed that PBS solutions (pH 9.0) could be used for Ti₃C₂@Fe₃O₄@β-CD regeneration, and the desorption percentage was above 70%. The molecular structure of DOX contains −OH and −NH₂ groups, which can form hydrogen-bonding interactions with C=O and −OH groups on the surface of Ti₃C₂@Fe₃O₄@β-CD. With pH increased, the hydrogen-bonding interaction was broken, which may result in the desorption of DOX from the surface of Ti₃C₂@Fe₃O₄@β-CD. The adsorption percentage remained in the range of 41.05−44.09%, and RSD based on the adsorption percentage through five replicate adsorption and desorption process was 2.8%. The desorption and regeneration results indicated that Ti₃C₂@Fe₃O₄@β-CD can be employed as a kind of recyclable adsorbents for DOX adsorption.
3.6. Interference Experiments. The interference on the adsorption of DOX was investigated when Na⁺, Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, and Ca²⁺ ions as the interfering ions coexisted with DOX in solution. The tolerance of interfering ions is defined as a 5% reduction in signal intensity. Results in Table 5 showed that the interfering ions cause no significant interference with the determination of DOX of 5 µg mL⁻¹ at pH 7.0. This is probably because the chemisorption based on host–guest interactions and hydrogen-bonding interactions are the primary adsorption.

3.7. Comparison of Ti₃C₂@Fe₃O₄@β-CD Performance with the Other Adsorbents. The comparisons of Ti₃C₂@Fe₃O₄@β-CD with other adsorbents for adsorption of DOX are summarized in Table 6. Higher adsorption capacities of some other’s work are related to the higher initial concentration and more adsorbent dosage used in these studies than the presented work. However, the proposed method can offer several advantages, including that it does not require any expensive instruments, complex preparation steps, and the operation is much easier.

4. CONCLUSIONS

The synthesis procedure and structural characterization of Ti₃C₂@Fe₃O₄@β-CD and then Ti₃C₂@Fe₃O₄@β-CD as an efficient adsorbent to adsorb DOX from aqueous solutions are reported in the present work. SEM analysis confirmed that the surface of Ti₃C₂ MXene was obviously an accordion-like structure. After preparing Ti₃C₂@Fe₃O₄@β-CD, a large number of regular spherical particles were uniformly immobilized in the structure of MXene nanosheets. XRD analysis confirmed that Ti₃C₂@Fe₃O₄@β-CD maintains the primary structure of Ti₃C₂ MXenes and Fe₃O₄. VSM analysis demonstrated that the prepared materials had magnetic properties and they could be readily separated from the reaction media. TGA analysis indicated that Ti₃C₂@Fe₃O₄@β-CD possessed remarkable thermogravimetric stability. The batch study confirmed that the adsorption of DOX onto the Ti₃C₂@Fe₃O₄@β-CD depended on the parameters such as pH, adsorption time, and initial concentration. Kinetic models and adsorption isotherms demonstrated that DOX adsorption fitted well to the pseudo-second-order kinetics models and Freundlich isotherm models. The thermodynamic study indicated that DOX adsorption onto the Ti₃C₂@Fe₃O₄@β-CD was endothermic, and the negative ΔG° values implied spontaneous adsorption. The positive value of ΔS° showed that randomness increased at the solid/solution interface. Moreover, Ti₃C₂@Fe₃O₄@β-CD could be effectively regenerated using a solution of PBS (pH 9.0). The adsorption percentage remained in the range of 41.05–44.09%, and RSD based on the adsorption percentage through five replicate adsorption and desorption process was 2.8%. These remarkable results indicated that Ti₃C₂@Fe₃O₄@β-CD possessed potential applications to adsorb DOX from aqueous solutions.

Table 5. Effect of Interfering Ions

| coexisting ions | tolerance limit/µg mL⁻¹ |
|----------------|------------------------|
| Na⁺, Cl⁻       | 1000                   |
| SO₄²⁻, NO₃⁻, CO₃²⁻, Ca²⁺ | 100               |

Table 6. Comparison of Ti₃C₂@Fe₃O₄@β-CD with Other Adsorbents Applied for Adsorption of DOX

| adsorbents                  | pH | initial concentration (mg mL⁻¹) | temperature (°C) | adsorbent dosage | adsorption capacity | adsorption time | ref             |
|-----------------------------|----|-------------------------------|------------------|------------------|---------------------|------------------|-----------------|
| GO@Fe₃O₄@ZnO@CS             | 7.0| 10                            | 25               | 0.01 g           | 390 mg g⁻¹          | 45 min          | 14              |
| green magnetic/graphene oxide/chitosan/alliumsativum/quercus nanocomposite | 6.3| 3                             | 25               | 1.4 g L⁻¹        | 32 mg g⁻¹          | 10 min          | 9               |
| Fe₃O₄ NPs                   | 6.0| 20                            | 30               | 0.5 g L⁻¹        | 10 mg g⁻¹           | 24 h            | 18              |
| Fe₃O₄@SiO₂-Glu              | 7.4| 20                            | 30               | 10 mg            | 64.51 mg g⁻¹       | 24 h            | 17              |
| Ti₃C₂@Fe₃O₄@β-CD            | 7.0| 5                             | 25               | 5 mg             | 7.35 µg mg⁻¹       | 60 min          | this work       |

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