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# Cationic Surfactant-Modified Covalent Organic Frameworks for Nitrate Removal from Aqueous Solution: Synthesis by Free Radical Polymerization

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**Abstract:** Development of efficient adsorbent is vital for nitrate removal due to the increasing nitrate contamination. Here we show a free radical polymerization strategy to prepare cationic surfactant-modified covalent organic framework (DhaTab-S) for removing nitrate from aqueous solution. The DhaTab-S was prepared by grafting a cationic surfactant diallyldimethylammonium chloride solution on vinyl-containing COF (DhaTab-V). The adsorption capacity for nitrate was pH dependent with the maximum at pH 6, and the adsorption process was largely influenced by ionic strength. The adsorption equilibrium for nitrate on DhaTab-S was reached within 40 min, following the pseudo-second-order kinetics. The DhaTab-S gave the adsorption capacity of 108.8 mg g<sup>-1</sup> for nitrate, being about 15 times adsorption capacity of the COF before surfactant modification. The large adsorption capacity makes DhaTab-S promising as sorbent for nitrate removal from aqueous medium.

The widespread use of nitrogen-containing fertilizers in agricultural production results in the excessive presence of nitrate and becomes a severe global environmental problem.<sup>[1-4]</sup> The high concentration of nitrate in surface and ground water can stimulate the excessive growth of aquatic plants and algae (eutrophication),<sup>[5-7]</sup> increase the incidence of digestive cancers once its reduction to nitrite<sup>[8-11]</sup> and give rise to blue baby disease (methaemoglobinemia).<sup>[12-14]</sup> Therefore, nitrate removal from contaminated aqueous medium is of great importance for environmental restoration.<sup>[15]</sup>

In recent years, several approaches have been developed to remove nitrate from contaminated water, including biological, chemical and physico-chemical treatments. Methanol and other organic substrates are usually involved in biological treatment.<sup>[16-18]</sup> Salinity, pH and temperature are often needed to be accurately controlled in chemical treatment.<sup>[19-23]</sup> Physico-chemical treatment including adsorption<sup>[24]</sup> and electro dialysis<sup>[25]</sup> is broadly used as the best method for nitrate removal.<sup>[26]</sup> As a

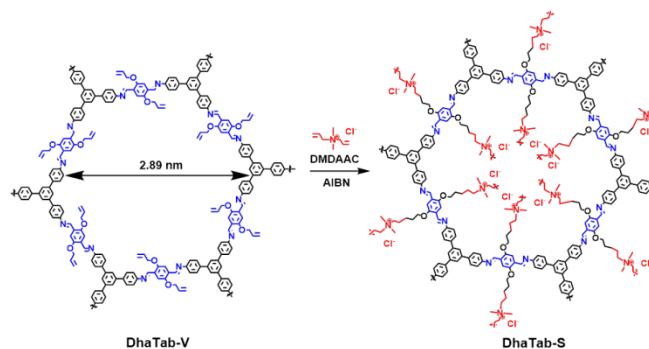
feasible method, adsorption has been widely applied in nitrate removal with the advantages of convenience, simplicity and efficiency.<sup>[27-31]</sup> Up to date, quite a few adsorbents such as zeolite and activated carbon<sup>[32-34]</sup> have been explored for nitrate adsorbents for nitrate removal is usually limited by the slow adsorption rate and low adsorption capacity due to the high solubility of nitrate.<sup>[2]</sup> Therefore, the design and development of efficient adsorbents is highly desirable.

Covalent organic framework (COF), a class of new porous materials, has many desirable merits including low density, porous structure, large surface area, facily tailored functionality, and high chemical stability.<sup>[35-37]</sup> Therefore, COF has attracted much attention and wide application in separation science.<sup>[38-41]</sup> Although COF has been used to remove heavy metals/radionuclides and organic pollutants,<sup>[42]</sup> its application in nitrate removal from water is still unreported. Additionally, the free radical polymerization method for the post-synthesis of functional COF is also unreported.

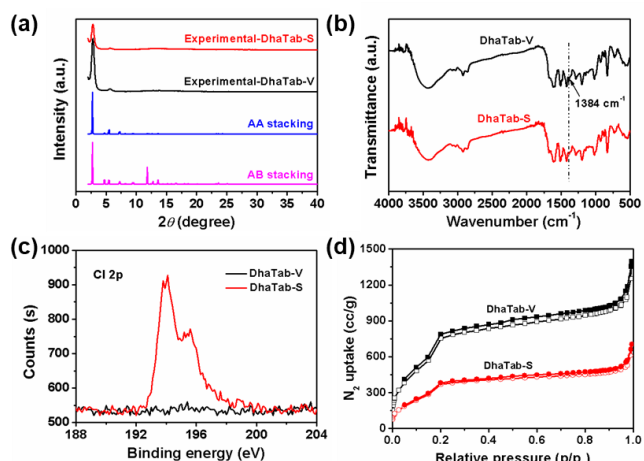
Herein, we report the preparation of cationic surfactant-modified COF via a post-synthetic strategy for the removal of nitrate from aqueous solution. The large adsorption capacity makes DhaTab-S promising as sorbent for nitrate removal. Figure 1 shows the preparation route of DhaTab-S. A vinyl-containing COF (DhaTab-V) prepared from 3,5-tris(4-aminophenyl)benzene (Tab) and vinyl modified 2,5-dihydroxyterephthalaldehyde (Da-V)<sup>[43]</sup> was used for further functionalization. Because of its advantages of high positive charge density, non-toxicity and low cost, vinyl-containing cationic surfactant diallyldimethylammonium chloride (DMAAC) was then covalently grafted onto DhaTab-V via free radical polymerization to prepare cationic surfactant-modified COF (DhaTab-S) under optimized conditions (Table S1). The performance of the prepared DhaTab-S for removing nitrate from aqueous solution was then demonstrated in detail.

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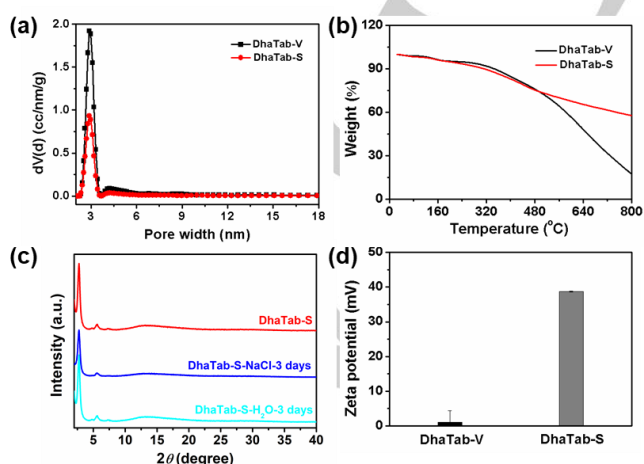
**Figure 1.** Scheme for the synthesis of DhaTab-S via free radical polymerization



**Figure 2.** Characterisation of DhaTab-S and DhaTab-V: (a) PXRD patterns; (b) FT-IR spectra; (c) Cl 2p XPS spectra; (d) N<sub>2</sub> adsorption-desorption curves.

The prepared DhaTab-S was characterised by powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) spectrometry, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The experimental PXRD pattern of DhaTab-V was better described by the eclipsed AA model than the AB stacking model (Figure 2a).<sup>[43]</sup> DhaTab-S showed the eclipsed AA crystal structure characteristic with two typical peaks at 2.8° and 5.6° as for DhaTab-V (Figure 2a),<sup>[43]</sup> but a partial loss of crystallinity due to the DMDAAC modification (Figure 2a). The introduction of DMDAAC to DhaTab-V led to a significant attenuation of the FT-IR stretching band for H<sub>2</sub>C=CH- (1384 cm<sup>-1</sup>) (Figure 2b), but gave a new XPS signal for chlorine and an enhanced XPS signal for nitrogen (DhaTab-S *cf.* DhaTab-V) (Figure 2c, Figure S1). The percentage of DMDAAC incorporated on the COF was evaluated to be 52.7% of the theoretical value based on the XPS results.

The modification of DMDAAC did not lead to obvious change in morphology (Figure S2), but significantly made the surface



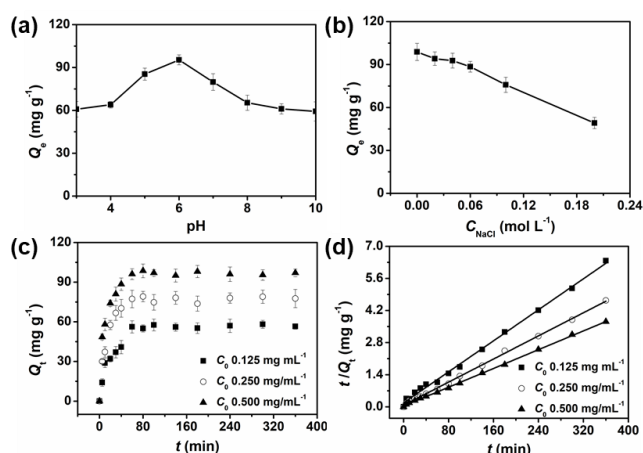
**Figure 3.** Characterization of DhaTab-S and DhaTab-V: (a) Pore size distribution; (b) TGA curves; (c) PXRD patterns of DhaTab-S in 40 mmol L<sup>-1</sup> NaCl solution and water for 3 days. (d) Zeta potential.

area decrease from 1753.3 m<sup>2</sup> g<sup>-1</sup> for DhaTab-V to 858.4 m<sup>2</sup> g<sup>-1</sup> for DhaTab-S (Figure 2d). Besides, the incorporated DMDAAC reduced the total pore volume from 1.57 (DhaTab-V) to 0.75 cm<sup>3</sup> g<sup>-1</sup> (DhaTab-S) (Figure 3a). The prepared DhaTab-S was thermally stable up to 300 °C as DhaTab-V (Figure 3b), and also stable in water/NaCl solution (40 mM) for 3 days (Figure 3c). The modification of DMDAAC gave more positively charged DhaTab-S (Figure 3d).

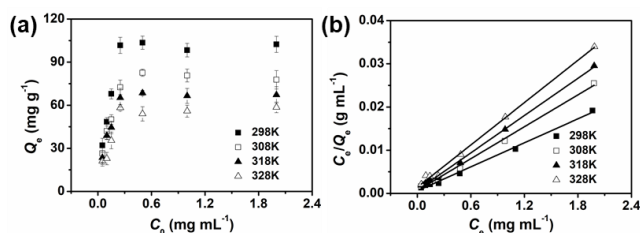
pH plays a crucial role in adsorption, impacting the property of adsorbent and target.<sup>[44]</sup> Thus, the effect of pH on nitrate adsorption was examined from pH 3 to 10 (Figure 4a). The adsorption capacity was pH dependent with the maximum at pH 6. The adsorption capacity decreased at pH < 6 likely because the increase of H<sub>3</sub>O<sup>+</sup> led to the decrease of effective concentration of nitrate ion.<sup>[1]</sup> However, DhaTab-S had more positive charge and more easily adsorbed nitrate ions at pH 6 via electrostatic interaction. The decrease of the adsorption capacity in basic conditions resulted from OH<sup>-</sup> for competitive adsorption on DhaTab-S. Hence, pH 6 was chosen for further study.

The effect of ionic strength was further investigated to show the role of ionic strength in the adsorption of nitrate. If electrostatic interaction is a dominated force between adsorbent and target, the adsorption process would be largely influenced by ionic strength.<sup>[45]</sup> To this end, the adsorption was carried out in the concentration range from 0 to 0.20 mol L<sup>-1</sup> NaCl (Figure 4b). The adsorption capacity for nitrate significantly decreased from 98.6 to 49.2 mg g<sup>-1</sup> as the NaCl concentration increased to 0.20 mol L<sup>-1</sup>, indicating that electrostatic interaction was a major mechanism for the adsorption nitrate on DhaTab-S. Hence, further study was carried out without NaCl.

The adsorption kinetics for nitrate on DhaTab-S was investigated for nitrate (Figure 4c). The adsorption of nitrate on DhaTab-S reached equilibrium within 40 min. The time-dependence of the adsorption capacity (Q<sub>t</sub>) for nitrate on DhaTab-S could be well described by the pseudo-second-order model (Figure 4d, Figure S3). The kinetic parameters calculated were summarised in Table S2.



**Figure 4.** (a) Effect of pH on nitrate adsorption with DhaTab-S. (b) Effect of NaCl concentration on nitrate adsorption with DhaTab-S. (c) Change of adsorption capacity for nitrate on DhaTab-S. (d) Pseudo-second-order kinetic plots for nitrate adsorption.



**Figure 5.** Adsorption isotherms (a) and Langmuir plots (b) for nitrate adsorption on DhaTab-S in the range of 298-328 K.

Adsorption isotherms for nitrate on DhaTab-S were measured in a series of nitrate solutions from 0.05 to 2.00 mg mL<sup>-1</sup> (Figure 5a). The adsorption capacity increased with nitrate concentration from 0.05 to 0.25 mg mL<sup>-1</sup> and reached equilibrium at 0.25 mg mL<sup>-1</sup>. The adsorption isotherms were well described by the Langmuir model (Figure 5b). The maximum adsorption capacity ( $Q_{\max}$ ) was 108.0 mg g<sup>-1</sup> (Table S3).

The adsorption energetics for nitrate adsorption was further studied from 298 to 328 K. Then, the free energy change ( $\Delta G$ , kJ mol<sup>-1</sup>), enthalpy change ( $\Delta H$ , kJ mol<sup>-1</sup>), and entropy change ( $\Delta S$ , J mol<sup>-1</sup> K<sup>-1</sup>) for the nitrate adsorption on DhaTab-S were calculated (Figure S4, Table S4). The results reveal that the nitrate adsorption on DhaTab-S is spontaneous ( $\Delta G < 0$ ) and exothermic ( $\Delta H < 0$ ) with decreased randomness ( $\Delta S < 0$ ).

The effect of coexisting anions on the nitrate adsorption on DhaTab-S was also tested. Typical anions, bromine, bicarbonate, sulfate and phosphate, were selected for this purpose. The coexisting anions had negative effect on nitrate adsorption, depending on coexistence anion (Figure S5). With similar spherical geometry to chloride provided by DMDAAC, bromine had minor effect on nitrate adsorption due to the steric or morphological effects.<sup>[15,46]</sup> However, other anions were non-spherical, e.g. nitrate and bicarbonate were trigonal while sulfate and phosphate were tetrahedral. Therefore, two/three adjacent binding sites were needed for sulfate and phosphate anions and the mono-valent ion nitrate and bicarbonate could fit more easily to the space on DhaTab-S.<sup>[15]</sup> As the result, bicarbonate had the larger negative effect on the nitrate adsorption than other anions.

Since the nitrate adsorption on DhaTab-S was attributed to electrostatic interaction, the presence of NaCl in solution would destruct electrostatic interaction, resulting in nitrate desorption. Therefore, the effect of NaCl concentration and desorption time on nitrate desorption was investigated. The results show that nitrate was efficiently desorbed from DhaTab-S with 40 mmol L<sup>-1</sup> NaCl for 10 min (Figure S6).

The adsorption of nitrate was examined on regenerated DhaTab-S to reveal its reusability. The adsorption capacity for nitrate and the zeta potential of the 4th regenerated DhaTab-S demonstrated the good reusability of DhaTab-S for nitrate removal (Figure S7 and Figure S8).

The prepared DhaTab-S gave about 15-fold improvement in the adsorption capacity for nitrate adsorption compared with DhaTab-V (Table S1), further revealing the necessity and effectiveness of incorporated surfactant onto COF via free radical polymerization. Additionally, DhaTab-S showed 1.5-13 times higher adsorption capacity than other adsorbents for nitrate removal (Table S5).

The prepared DhaTab-S was applied for removing nitrate from tap water to further demonstrate the feasibility for the application of DhaTab-S in real water samples. There was no significant difference in the experimental maximum adsorption capacity in tap water (99.0 mg g<sup>-1</sup>, Table S6) and in aqueous standard solution (108.0 mg g<sup>-1</sup>). The results indicate the feasibility of DhaTab-S as a promising sorbent for nitrate removal from tap water.

In summary, we have designed and developed a cationic surfactant-modified COF (DhaTab-S) via a free radical polymerization strategy. With the abundant charge of surfactant and large surface area, DhaTab-S provided more electrostatic interaction sites and sufficient contacting area for nitrate removal. The high adsorption capacity makes DhaTab-S a potential adsorbent for nitrate removal from tap water.

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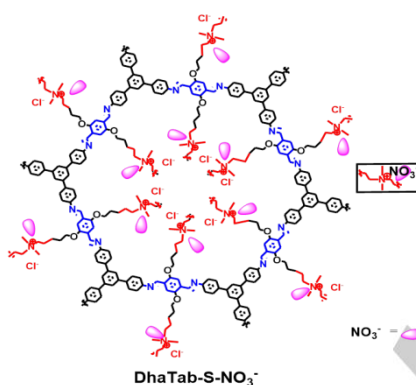
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## Entry for the Table of Contents

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