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Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.9b00671 • Publication Date (Web): 13 Aug 2019

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A Double-walled Thorium-based Metal-Organic Framework (MOF) as a Promising Dual Functional Absorbent for Efficiently Capturing Iodine and Dyes

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ABSTRACT: We prepared a rare Th-MOF (Th-TATAB) with a double-walled tetrahedral cage structure and giant unit cell volume 43513 Å^3 which is the largest of all reported thorium-based MOFs to our knowledge. The unique structure characters make the thorium-based MOF exhibits exceptionally adsorption properties toward I_2 and dyes with different charges. The experimental results show that in cyclohexane solution the absorption ability of Th-TATAB toward I_2 can reach about 750 mg/g, especially the removal efficiency in cyclohexane solution（0.01 mol/L） can reach 90% in 3 hours, which far exceeded that of reported $[Zn_2(tptc)\text{-}(apy)_{2-x}(H_2O)_x]\cdot H_2O$

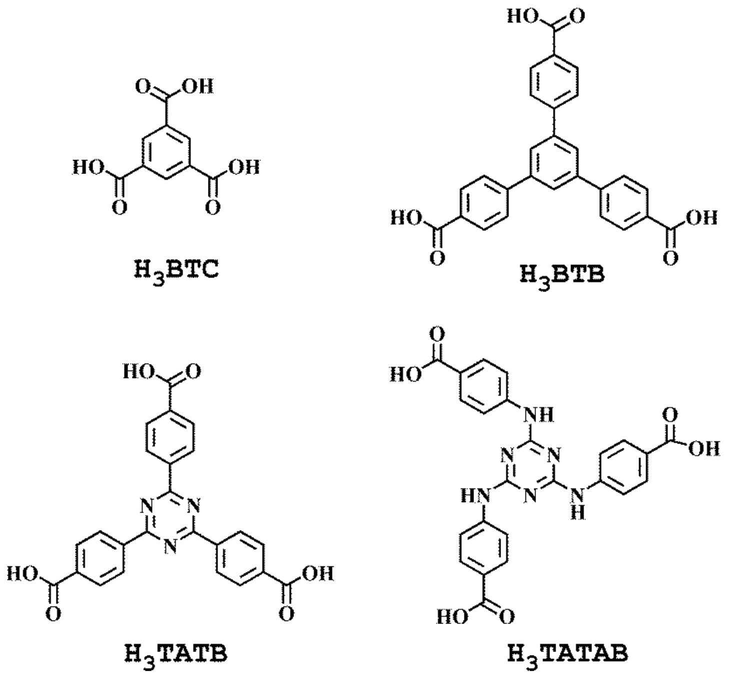
(80%, 48 h) and MIL-101-NH_2 (90%, 30 h). Furthermore, the simultaneous removal of molecules with different charges is very challenging, while Th-TATAB displays excellent adsorption properties for anions, neutral and cations dyes individually and simultaneously from aqueous solution. The exploration of the adsorption performance of MOF Th-TATAB for iodine in cyclohexane solution and dye contaminants in aqueous solution is of great significance in environmental aspect, which provided a new strategic idea for opening up the potential applications of thorium-based MOF and understanding actinides chemistry.

INTRODUCTION

Nowadays, metal-organic frameworks (MOFs) have attracted much interest due to its extensive application in many realms such as adsorption,[1] separation,[2] sensing,[3] proton conduction[4] and heterogeneous catalysis.[5] Among them, the application of MOF as a functional adsorbent to effectively capture various analysts such as drugs, explosives, dyes contaminants and radioactive wastes, has a broad prospect.[6-7] MOFs based thorium stand for a small part of the MOF family, which are less developed and explored comparing to MOFs constructed by transition and lanthanide. Compared with other high valent metal cations (such as zirconium (IV) or cerium (IV), tetravalent acts such as thorium (IV) have wider coordination numbers and exhibit more various coordination environments. [8-9] Since O'Hare *et al.* firstly constructed Th-MOF $[(Th_2F_5)(NC_7H_5O_4)_2(H_2O)][NO_3]$ using $Th(NO_3)_4 \cdot 6H_2O$ and pyridinedicarboxylate in 2003,[10] researchers have made more efforts to develop Th-MOFs with rich structure to deeply understand thorium chemistry for nuclear science, and the progress made in this field is very encouraging. [10-18] Knope *et al.* prepared two isomorphous compounds $Th_6O_4(OH)_4(H_2O)_6(4-$

hydroxybenzoate)$_{12}$]$\cdot$nH_2O and [$U_6O_4(OH)_4(H_2O)_6$(4-hydroxybenzoate)$_{12}$]$\cdot$nH_2O and studied the effect of organic skeleton on the solution and solid-state structural chemistry of thorium-uranium complexes.[18] Christopher *et al.* synthesized a novel Th-MOF Th[4,4′-oxybis(benzoic) aci]$_2$, which exhibited excellent chemical and thermal stability.[16]

Iodine, as one of the volatile radionuclides, is an important issue in nuclear waste management. Efficiently capturing iodine is still very challenging due to high fluidity and low adsorption capacity of its species. Recently, porous MOFs as a new kind of adsorbents, have been utilized to capture I_2, showing excellent adsorption capacity.[19-20] Thallapally *et al.* synthesized two microporous MOFs SBMOF-1 [Ca(4,4′-sulfonyldibenzoate)] and SBMOF-2 [Ca(1,2,4,5-tetrakis(4-carboxyphenyl)-benzene)] according to the literature and studied their adsorption properties for iodine under humidity conditions.[20] A feasible method for constructing MOF with good affinity for I_2 is to introduce conjugated π-electron organic linker, that can generate stable charge-transfer (CT) complexes or halogen bonds with I_2, therefore enhancing the adsorption capacity for iodine adsorption.[21] Moreover, some conjugated triazine-based frameworks (CTFs), also called 1,3,5-triazine-based conjugated microporous polymers (TCMPs), have also been developed for I_2 capture.[22] Since the existence of triazine heterocyclics with rich nitrogen atoms in CMPs systems dramatically enhance their I_2 binding affinity and heighten the interaction between the adsorbates and adsorbents, TCMPs possess excellent iodine capture capacities at ambient pressure.[6, 22-24] So, it is significant to think over that the 1,3,5-triazine heterocycle containing polycarboxylate groups with multiple conformations and bonding modes in the selection or design of organic ligands. For one thing, it is an extraordinary aromatic component that can lead to p–p stacking and anion–p interactions.[23-24] For another, the triazine ring contains three nitrogen atoms, which not only coordinate with metal ions, but also form a variable network structure.[25-27] In the large family of triazine polycarboxylate acids, trigonal tricarboxylate ligand H_3TATAB containing amino functional group is a typical representative. Compared with the other triangular tricarboxylic acid linkers, such as BTC, BTB and TATB, its structure is more extended. (Scheme 1). Many novel high-porosity MOFs have been formed by assembling TATAB ligands with transition metals and rare earth ions, which exhibited excellent performance in areas such as luminescent sensing and adsorption.[28-30] In addition, organic dye contaminants in water are also a serious problem because they are usually stable, toxic and potentially carcinogenic, even severely threatening to ecological environment. Hence, the efficient adsorption removal of dye contaminants from water is crucial. Due to the diverse topologies, high porosity, adjustable aperture, and unique host-guest interactions, MOFs has been extensively investigated for the efficient removal of organic dye pollutants from wastewater.[25, 31-34] Especially many MOFs show excellent performance in selective adsorbing dyes.[34-37] For example, Hong *et al.* constructed an anionic uranium-based MOF $[(CH_3)_2NH_2]_4[(UO_2)_4(TCPE)_3]\cdot(\text{solvent})_x$, showing excellent adsorption performance for cationic dyes Ethyl Violet, Rhodamine B and Janus Green B.[25] Liu *et al*. presented a 1D rare earth compound $\{[(CH_3)_2NH_2]\ [(H_2abtc)_2Ho(H_2O)]\}n$, which showed a high removal efficiency of positively charged dyes methylene blue.[35] Xing *et al.* assembled a unique two-dimensional uranyl complex $[(CH_3)_2NH_2][UO_2(TATAB)]\cdot 2DMF\cdot 4H_2O$ by using triazine tricarboxylic acid ligand, which featured 2D graphene-like topological structure and displayed selective adsorption ability to cationic dyes Safranine T and methylene blue.[26] However, simultaneous removal of anionic and cationic dyes/anionic, neutral and cationic dyes from water solutions is still a challenge. The development of the dual functional absorbent for iodine and dye is very promising and significant. Herein, we adopted high-valence Th(IV) cation and conjugated π-electron ligand H_3TATAB to successfully assemble a novel dual-function MOF Th-TATAB and firstly explored its sorption properties for I_2 and dye molecules.



Scheme 1. Structure of Some Trigonal Tricarboxylic Ligands.

EXPERIMENTAL SECTION

Caution! *Thorium is a chemically toxic and radioactive element, standard precautionary measures to handle radioactive substances ought to be followed.*

Synthesis of Ligand 4,4',4"-s-triazine-1,3,5-triyltri-p-aminobenzoate (H_3TATAB). Ligand H_3TATAB was synthesized according to the literature and slightly modified.[28,38] 4-aminobenzoic acid (4.5 g, 33 mmol), NaOH (1.5 g, 37.5 mmol), and $NaHCO_3$ (2.25 g, 27.5 mmol) were placed in 50 mL of deionized water. At 0 ºC, stir the mixed solution for 30 min. Cyanuric chloride (1.5 g, 8.25 mmol) was added to 1,4-dioxane (15 mL) and stirred until dissolved, then dripped into the above mixed solution. The mixed solution was then refluxed for 24 h in an oil bath at 115 ºC. The obtained solution was acidified with 20% hydrochloric acid to pH=3. The light yellow product was obtained by filtration, washed with distilled water until neutral, and dried to gain ligand H_3TATAB (4.5 g, yield: 80%). ^{1}HNMR (d_6-DMSO, 400 MHz): δ=7.88 (d, 6H), 7.97 (d, 6H), 9.84 (s, 3H), 12.64 (s, br, 3H). The ^{1}H-NMR spectra of the ligand H_3TATAB is presented in Figure S1.

Synthesis of MOF Th-TATAB, $Th_6O_4(OH)_4(H_2O)_6(TATAB)_2(HCO_2)_6$. A mixture of $Th(NO_3)_4\cdot6H_2O$ (0.05 mmol), H_3TATAB (0.05 mmol)m, DMF (4 mL) and H_2O (1mL) was stirred at room temperature for 20 min. The mixed solution was adjusted to pH=3 with nitric acid (4 mol/L), then transferred to 20 mL Teflon-lined stainless steel autoclave and heated for 2 days at 160 ºC. After cooling, filtering and washing with DMF, colorless octahedral crystals are obtained, yield 57 % (14 mg, based on metal). The formula of the crystal is $Th_6O_4(OH)_4(H_2O)_6(TATAB)_2(HCO_2)_6$, which was confirmed by X-ray single crystal diffraction analysis, Elemental analysis (% calc/found: C 22.63/23.04, H 1.68/1.77, N 5.87/5.99), and TGA (before 400 ºC weight loss of 30 wt%).

Single Crystal X-ray diffraction Determination. Single crystals with appropriate sizes of MOF Th-TATAB were mounted on glass fibers to collect X-ray diffraction data. The determination of crystal structure were performed on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. A semiempirical absorption correction was applied by the program SADABS.[39] Single crystal structure was solved by direct methods and refined by full-matrix least squares on

F^2 using the SHELX-97 program.[40-41] All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic data are summarized in Table 1. The selected bond distances (Å) are given in Table 2.

Table 1. The crystallographic data for Th-TATAB

Compound	Th-TATAB
Molecular formula	$C_{54}H_{48}N_{12}O_{38}Th_6$
formula weight	2865.28
T (K)	293
Crystal system	cubic
Space group	*Fd-3*
a (Å)	35.1727(7)
b (Å)	35.1727(7)
c (Å)	35.1727(7)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	43512.8(15)
Z	16
D, g/cm^{32}	1.750
F(000)	20800.0
Goodness of fit on F^2	1.232
Final R indices [$I > 2\sigma(I)$]	R_1=0.0925 , wR_2=0.1612

Final *R* indices (all data)	R_1=0.1538 , wR_2=0.1828

Table 2. Selected bond lengths (Å) for Th-TATAB

Selected bond lengths (Å)			
Th1-O1	2.459(12)	Th1-O2	2.429(11)
Th1-O3	2.45(2)	Th1-O4	2.381(8)
Th1-O5	2.806(16)	Th1-O6	2.566(18)
Th1-O7W	2.512(18)		

Capture of iodine experiments in cyclohexane solution. At room temperature a few samples 100 mg of Th-TATAB were respectively added to cyclohexane solution dissolved with iodine (0.01, 0.02, 0.03 and 0.04 mol/L). Ultraviolet-visible absorption spectroscopy was applied to monitor the kinetics of iodine adsorption by MOF.

Release of iodine experiments in ethanol solution At room temperature, a few samples 20 mg of Th-TATAB were put into iodine-dissolved cyclohexane solution (100 mgL^{-1}, 5 mL) for 24 hours to prepare the iodine-loaded sample. Then 20 mg of composite I_2@Th-TATAB were soaked in ethanol (10 mL). The residual concentration of iodine solution was measured by ultraviolet-visible spectrometer at room temperature.

Adsorption experiments in a single dye solution 5 mg of Th-TATAB were added into 5 mL of the water solution containing methyl orange, Eosin Y, alizarin , rhodamine B and methylene blue at room temperature, the initial concentration of which is 10 mgL^{-1}. Supernatant solutions were taken from the suspensions with a syringe as samples for analyses after 0, 1, 2, 3, 4, 6, 8 10 and

23 h. Monitor the residual concentration of the dye-containing solution with ultraviolet-visible spectrophotometer at the absorbance (λ_{max}) of each dye supernatant.

Effect of initial concentrations on adsorptive removal of methyl orange. 5 mg of Th-TATAB were immersed into 5 ml of aqueous solution containing methyl orange at different initial concentrations (10, 20, 30 mgL^{-1}). The maximum absorbance change of methyl orange dye solution at different initial concentrations was respectively recorded by an ultraviolet-visible spectrophotometer at room temperature. Subsequently, 5 mg of Th-MOF was separately soaked in solution containing methyl orange (40, 60, 80 and 100 mgL^{-1}). After a week, the residual concentration of the above solution was respectively recorded by an ultraviolet-visible spectrophotometer to obtain the dye removal efficiency and equilibrium adsorption amount. The formula of the dye removal efficiency is expressed as follows:

$$\% \text{ Removal} = [(C_0 - C_t)/C_0] \times 100$$

where C_0 is the initial concentration of the dyes, and C_t is the concentration of dyes at any specified time.

RESULTS AND DISCUSSION

Crystal Structures. Solvothermal reaction of trigonal ligand H_3TATAB and thorium nitrate in the presence of DMF, H_2O and HNO_3 at 160 °C 48 h yielded colorless octahedral crystals of Th-TATAB (Figure S2). Structural analysis shows that Th-TATAB crystalizes in the cubic system with the space group *Fd-3*. It was formulated as $Th_6O_4(OH)_4(H_2O)_6(TATAB)_2(HCO_2)_6$ by the characterization of IR, PXRD, TG, single-crystal X-ray diffraction, and elemental analysis. The crystal structure of MOF Th-TATAB is based upon inorganic building unit $Th_6O_4(OH)_4(CO_2)_{12}$ (Figure 1b) which is similar to $Zr_6O_4(OH)_4(CO_2)_{12}$ brick from UiO-66. Unlike UiO-66 with linear linker BDC, this thorium-based MOF Th-TATAB is formed with the trigonal ligand TATAB. The inorganic building brick is comprised of the inner $Th_6O_4(OH)_4$ core (Figure 1a), in which six thorium atoms form a Th_6-octahedron and are located at the vertices of the octahedron. All triangular faces of the octahedron are alternately capped by the μ_3-O and μ_3-OH which share three thorium centers. The edges of octahedron are bridged by carboxylates ($-CO_2$) from the TATAB ligand and formic acid which is derived from DMF decomposition. Each thorium center is coordinated by three types of oxygen atoms, defining a monocapped square antiprismatic polyhedron. Four of them originate from carboxyl oxygen atoms of trigonal ligand TATAB and formic acid; Four other oxygen atoms are supplied the groups of by μ_3-O and μ_3-OH; And the terminal oxygen atom corresponds to the coordinated water molecule. The distances of Th-O bond for Th-μ_3O(H), Th-O_{TATAB}, Th-O_{HCOO} and Th-O_{water} of 2.3787, 2.4409, 2.5341, and 2.7967Å respectively, are typical in nine-coordinated complexes containing thorium(IV). The presence of μ_3-O(H) groups meet the requirements of charge balance, which has been previously reported in other complexes with hexanuclear Th-cluster structures.[12, 42] Average bond value for Th-μ_3(O,OH) (2.3787Å) is comparable with Th-μ_3(O,OH) bond value of 2.391Å for the previously reported compound $Th_6(OH)_4O_4(H_2O)_6(OAc)_{12}\cdot nH_2O$.[42] Although Th-$O_{water}$ bond value of 2.7967Å is relatively long, it is comparable to that of several thorium(IV) complexes reported in the literature.[11, 13] Each trigonal tricarboxylate ligand are linked three inorganic brick (Figure 1c), and each inorganic building brick is connect with six trigonal tricarboxylate ligand TATAB(Figure 1d). The inorganic building brick are linked each other through the trigonal tricarboxylate linker TATAB to form truncated tetrahedral cavities with a size of 17 Å（Figure

1e and 1f). Interestingly, Th-TATAB is a very rare double-walled MOF, the double-walled tetrahedron cage of which is formed by the interlacing of two triangular ligands connected with inorganic brick.

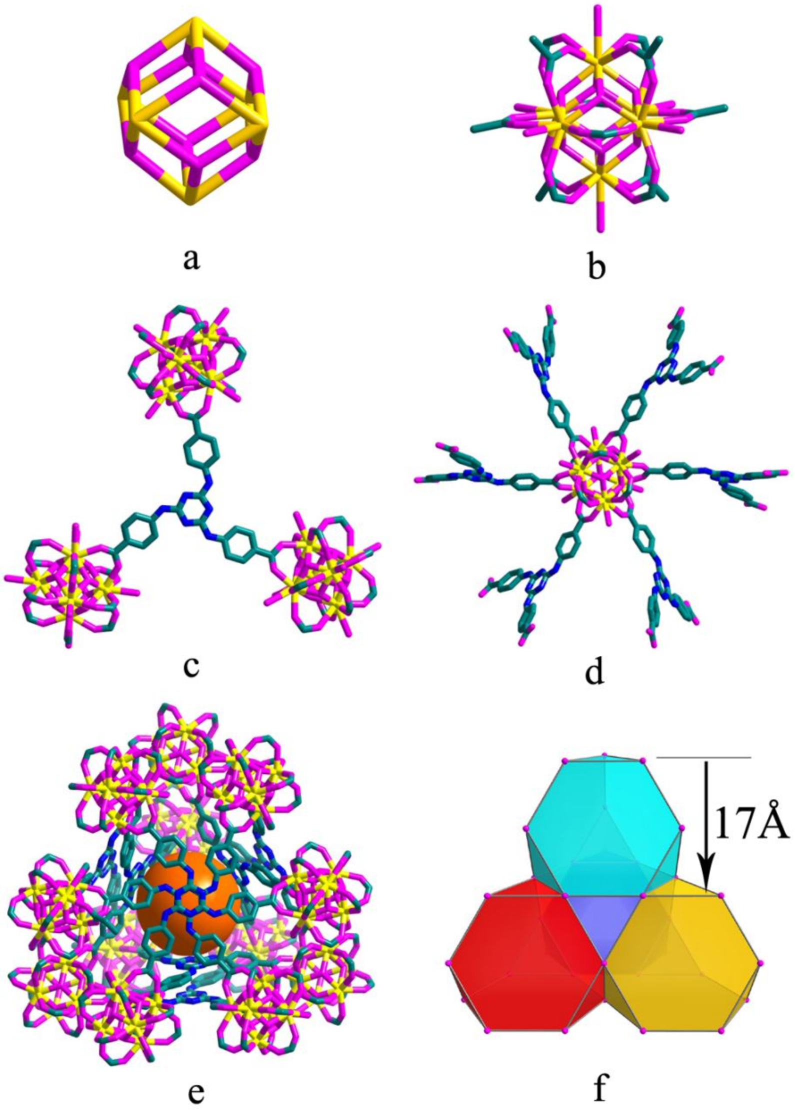


Figure 1. Structural features of Th-TATAB: (a) The inner core $Th_6O_4(OH)_4$ of Th-TATAB; (b) The inorganic building brick; (c) Ligands TATAB connecting three inorganic building brick; (d) The inorganic building brick linked six ligands TATAB. (e) The truncated tetrahedral cage in Th-TATAB. (f) Graphical representation illustrating the

interconnected cages with 17Å diameter. For clarity hydrogens atoms and solvent molecules are omitted. Atom color codes: thorium, yellow; oxygen, pink; carbon, teal; nitrogen, blue.

Capture and Release of Iodine Iodine uptake of Th-TATAB was investigated in cyclohexane solution. We first explored the effect of different initial concentrations on iodine removal efficiency. (Figure S13). At room temperature a few samples 100 mg of Th-TATAB were separately soaked in 5 mL cyclohexane solution dissolving iodine (0.01, 0.02, 0.03 and 0.04 mol/L). Iodine adsorption process was monitored by UV-visible spectroscopy. After 24 h, the removal efficiencies of 99.9%, 99.1%, 97.2% and 93.1% were achieved respectively for iodine cyclohexane solution of 0.01, 0.02, 0.03 and 0.04 mol/L, respectively (Figure 2a). The MOF sample was immersed in a cyclohexane solution dissolving iodine at room temperature. After about 24 hours, the dark purple solutions of iodine gradually faded to pale (Figure 2a insets), which demonstrated that the I_2 was encapsulated in the skeleton of Th-TATAB so that in solution a system loaded with iodine is successfully produced.[43] Especially, when I_2 solution is 0.01 mol/L, the removal efficiency of iodine by Th-TATAB can reach 90% in 3 hours, which far exceeded that of reported $[Zn_2(tptc)\text{-}(apy)_{2-x}(H_2O)_x]\cdot H_2O$ (80%, 48h) and MIL-101-NH_2 (90%, 30h).[44-45] As shown in Figure 2d, after 72 hours, the adsorption capacity of Th-TATAB for iodine reached approximately 700 mg/g and 750 mg/g when 10 mL and 15 mL of iodine solution (0.04 mol/L) were added, respectively, while the iodine-loaded crystals turned black (Figure 2d inset). In order to study the influence of different contact time on iodine adsorption capacity, an in-depth analysis can be performed by fitting pseudo-second-order model (Figure 2b). Obviously, the kinetic process of iodine adsorption by MOF Th-TATAB is well described by pseudo-second-order kinetic model. The affinity and strong adsorption capacity of MOF Th-

TATAB for iodine can be put down to the plentiful phenyl rings, high porosity, and the structural features of the π-electron walls constructed by TATAB, which can be explicated in the following aspects. First, iodine is adsorbed inside the pores of MOF Th-TATAB through I–I···N bonds and I–I···π halogen bonds.[46] Moreover, the underlying intermolecular interactions between iodine molecule and π-electron double-walls are crucial, because the single path for iodine molecules is allowed to entry and be restricted in well-regulated narrow limits in the nanochannels, resulting in n→σ*charge transfer (CT).[47]

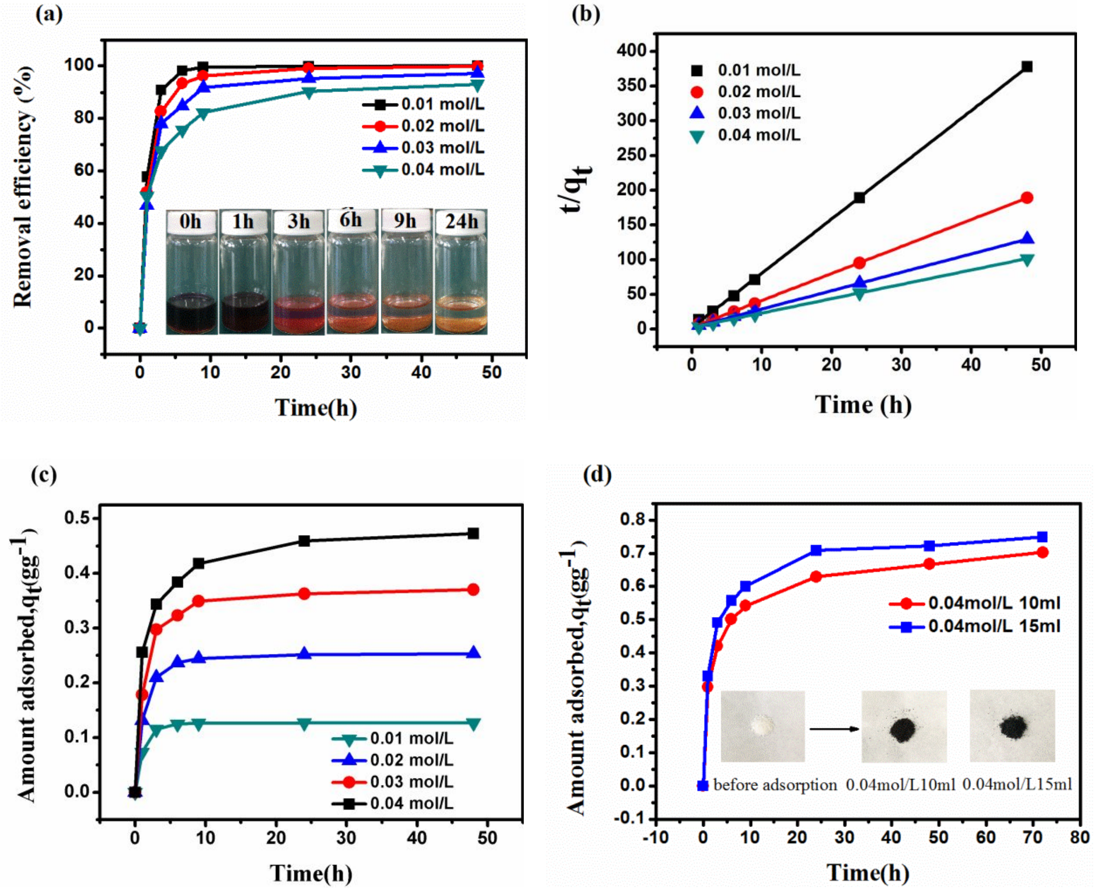


Figure 2. (a) The removal efficiency of MOF Th-TATAB for iodine when the initial concentration of iodine in cyclohexane solution is 0.01, 0.02, 0.03 and 0.04 mol/L.; The insets show the color change of iodine solution during iodine enrichment; (b) Plots of pseudo-second-

order kinetics; (c) The adsorption capacity of MOF Th-TATAB for iodine when the initial concentration of iodine in cyclohexane solution is 0.01, 0.02, 0.03 and 0.04 mol/L; (d) The adsorption capacity of iodine when 10 mL and 15 mL iodine solution (0.04mol/L) was added respectively.

In the meantime, the release of iodine from iodine-loaded samples I_2@Th-TATAB was determined by UV-vis spectra (Figure 3 and S1). The release rate was rapid during the first day, and no significant change was observed after 3 days, indicating that the release reached equilibrium (Figure 3b). After 7 days, about 85.64% of the initial I_2 had been released from I_2@Th-TATAB, showing the adsorption process of MOF Th-TATAB toward I_2 is reversible (Figure 3b). We deem that host-guest interaction plays a key role in such release behavior.[48] Strong π-electron-iodine and host-guest interactions promote I_2 uptake, whereas it would also undermine the desorption of I_2 from I_2@Th-TATAB, leading to the incomplete delivery of iodine from I_2@Th-TATAB composite system.[49] Because of the skeleton collapse of the sample after methanol activation (Figure S3b), the unactivated sample was used for the measurement of nitrogen adsorption. It is possible that due to the guest molecule in the MOF pore could not be removed effectively, the ideal result of nitrogen adsorption measurement was not obtained, although the void space predicted by the PLATON calculation is 42.1%.

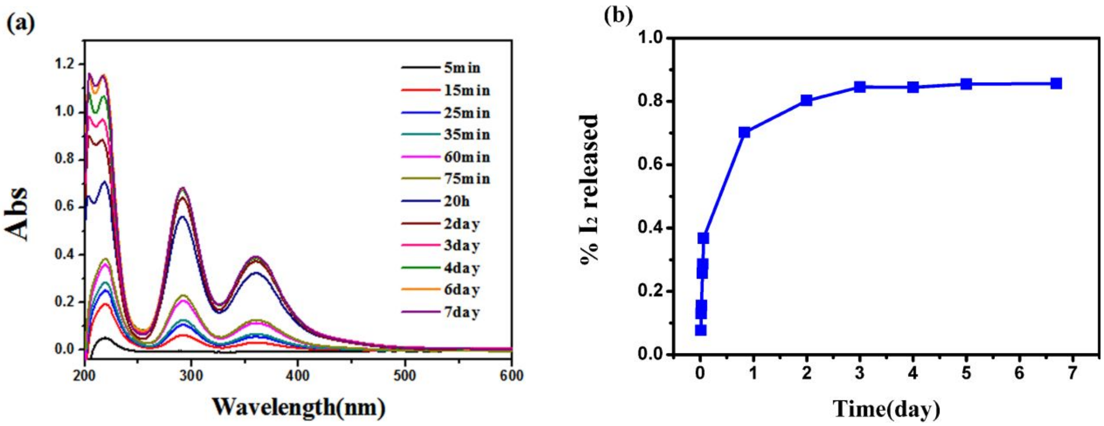
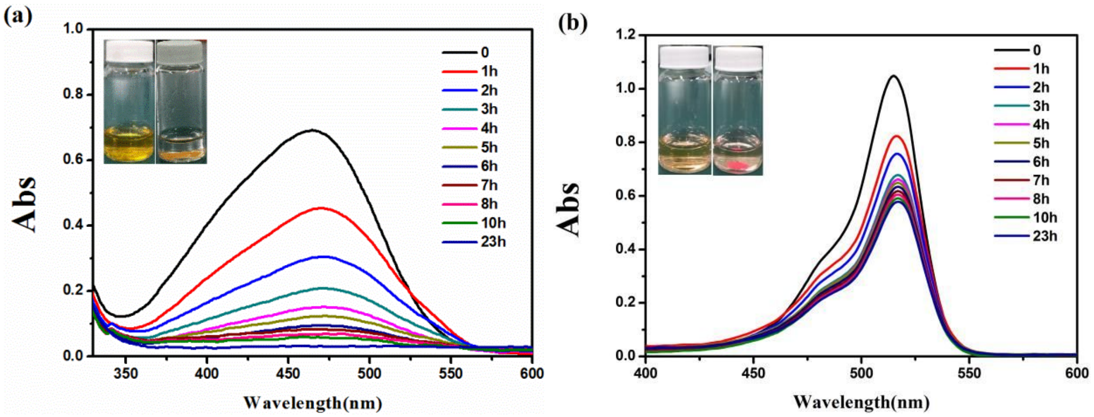


Figure 3. Kinetic plot of iodine delivery from the composite I_2@Th-TATAB measured by UV-vis absorption spectra in ethanol solution.

Dye adsorption. Based on the pore size (17Å) of the tetrahedral cavity of MOF Th-TATAB, five dyes with suitable dimensions for pore permeation (molecular size < 1.7 nm): negatively charged methyl orange {4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt}, Eosin Y [disodium2-(2,4,5,7-tetrabromo-6-oxido-3-oxoxanthen-9-yl)benzoate]; electrically neutral alizarin [1,2-Dihydroxyanthracene-9,10-dione]; and positively charged rhodamine B [9-(2-carboxyphenyl)-3,6-bis(diethylamino)xanthylium chloride] and methylene blue [3,7-Bis(dimethylamino)-5-phenothiazinium Chloride] (Figure S14) were chosen to evaluate the adsorption ability of Th-TATAB in a dye-containing aqueous solution. The complex all exhibits adsorption behavior to anionic, neutral and cationic dye molecules to some extent (Figure 4), in which the removal efficiency of anionic dye MO (96%) is the highest. In the same charged dye solution, the Th-MOF has higher adsorption efficiency for linear dye MO (96%) than the triangle dye molecule Eosin Y (44%); the uptakes toward the linear MB (34%) were more efficient than triangle dye molecule rhodamine B (20%). This observed result indicates that the anionic, neutral and cationic dye molecules with appropriate size to accommodate nanotube channels of the Th-TATAB frame can be adsorbed and entered into the pores of MOF. The adsorptive behavior of

Th-TATAB on dyes does not only exhibit size and shape dependence, but also charge dependence to a certain extent. In the same charged dye solution, the Th-MOF has higher adsorption efficiency for linear dye molecule methyl orange than the triangle dye molecule Eosin Y; the uptakes toward the linear methylene blue were more efficient than triangle dye molecule rhodamine B. We believed that the difference in adsorption between dye molecules with the same charge may be due to shape effects. In order to further confirm our inference, another linear anionic dye Orange II [4-(2-Hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt] was selected for adsorption experiments. The experimental results show that the Th-MOF also exhibits a high adsorption capacity for linear anionic dye molecule Orange II (Figure 4c), which is comparable to that for linear dye molecule MO, and significantly higher than that for triangular dye molecule Eosin Y. Therefore, the experimental results are consistent with expectations. Compared with the triangular dye molecules, linear dye molecules are more acceptable to access to the pore of the MOF; Whereas the difference in adsorption between dye linear dye molecules MO, alizarin and MB may be due to charge dependence.



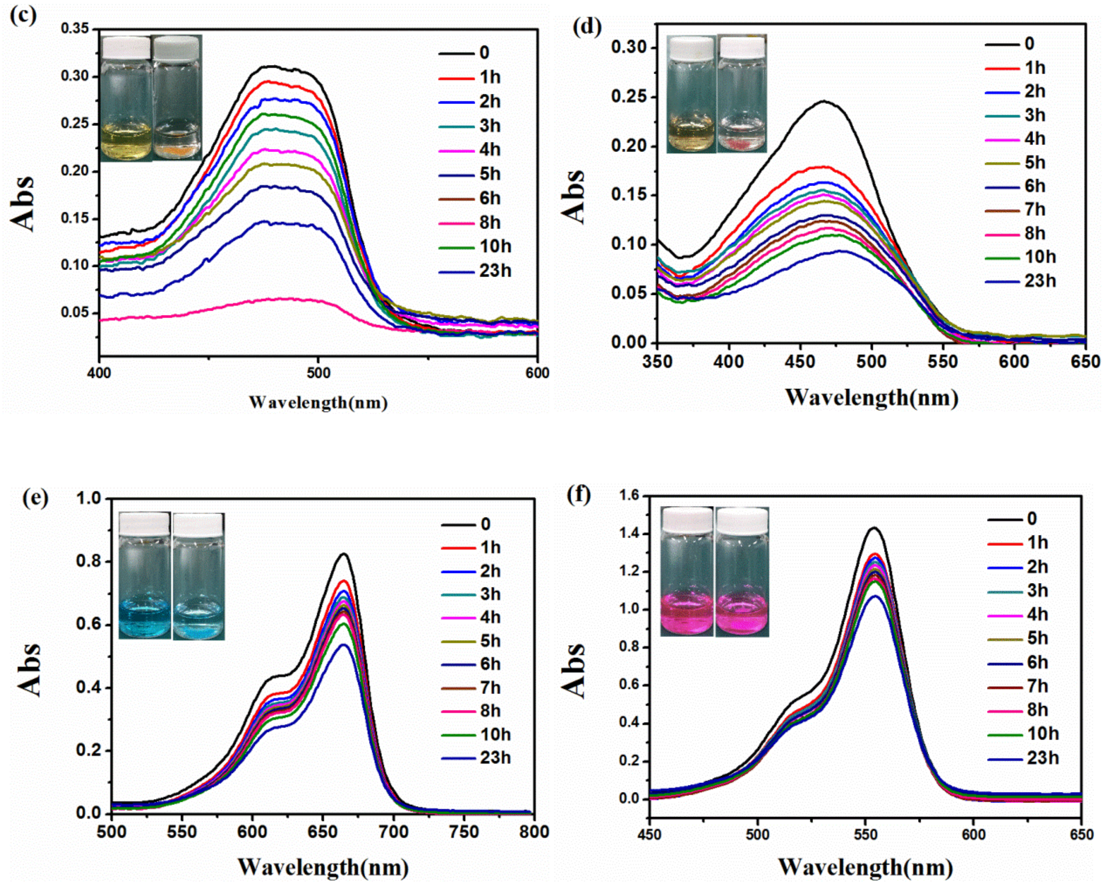


Figure 4. UV-visible absorption spectrum of the single dye solution. (a) MO, (b) Eosin Y, (c) alizarin, (d) MB and (e) rhodamine B. The insets show the change in color of the dye solution after adsorption.

Considering the excellent adsorption performance of Th-TATAB for MO, we further explored the influence of different initial concentration on the dye removal by Th-TATAB (Figure S15). The removal efficiency of methyl orange solution at three different initial concentrations (10, 20, and 30 mgL^{-1}) can achieved 96%, 98% and 97% respectively after 23 hours;the adsorption amount can reached 9.79, 19.97 and 29.99 mg/g, respectively after 23 hours (Figure 5b). Moreover, in order to further study the influence of different contact time on adsorptive behavior of Th-TATAB toward MO, linear fit was conducted using the pseudo-second-order kinetic model (Figure 5a and Table 3). Obviously, for methyl orange dye solution of different initial concentrations, the pseudo-second-order kinetic equation has a good fitting degree, which can well describe the kinetic process of Th-TATAB adsorbing methyl orange dyes.

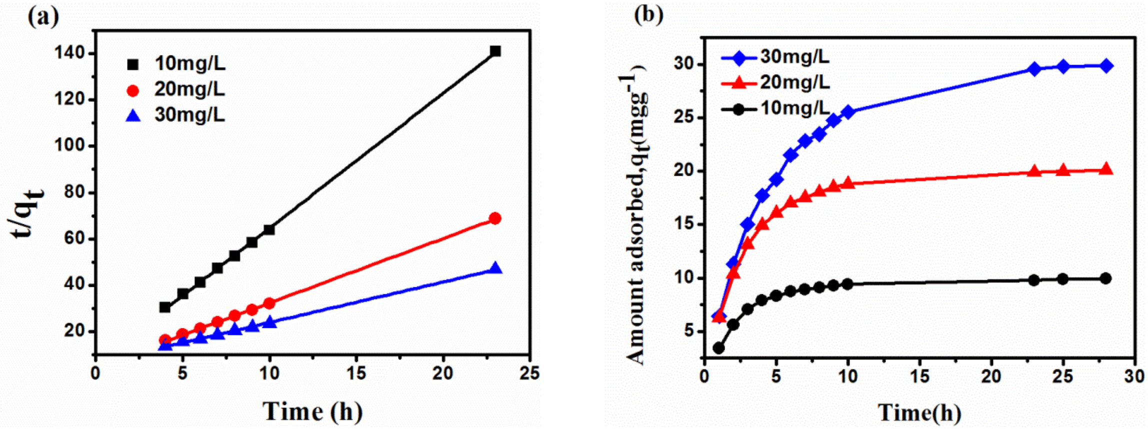


Figure 5. (a) Linear regressions of MO; (b) The adsorption ability of MOF Th-TATAB for MO when the initial concentration of the solution is 10, 20 and 30 mgL^{-1}.

Table 3. Adsorption kinetic parameters of MO on Th-TATAB

Dye	C_0 (mg L^{-1})	pseudo secondary-order kinetics		
		k_2 (g mg min^{-1})	R^2	q_e (mg g^{-1})
MO	10	9.724×10^{-2}	0.9978	9.79
	20	4.643×10^{-2}	0.9981	19.97
	30	2.919×10^{-2}	0.9982	29.99

Subsequently, the adsorption capacity of the Th-MOF was monitored when the initial concentration of methyl orange dye solution was 40, 60, 80 and 100 mgL^{-1}

respectively (Figure S17 and 6). It can be seen that the initial concentration of the solution is a key factor affecting the amount of adsorption. As the initial concentration increases, the equilibrium adsorption amount gradually increases, reaching a maximum value of 99.53 mg/g at the initial concentration of 100 mgL^{-1}.

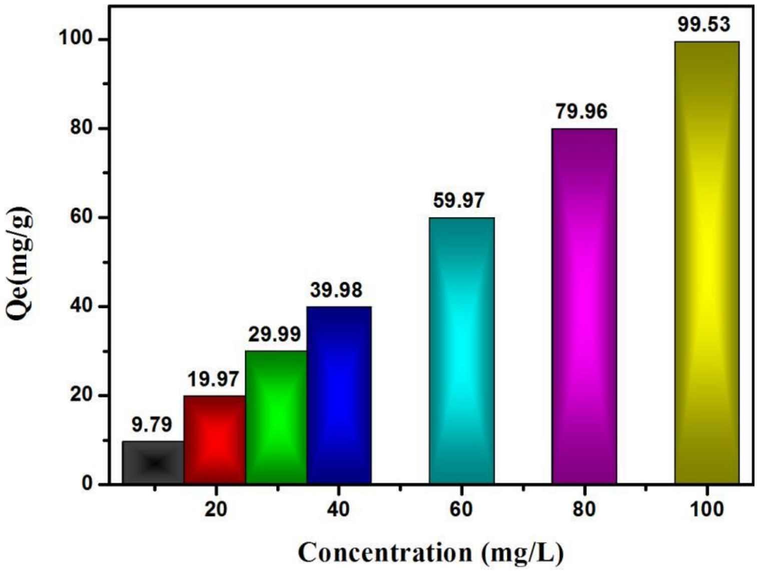


Fig 6. The influence of different initial concentration on the adsorption capacity of Th-MOF toward MO.

Many MOFs show selective adsorption behavior for cationic or anionic dyes, and there are many reports about this aspect,**[32, 50]** while the simultaneous removal of molecules with different charges is still very challenging.[51] In this paper, the adsorptive behavior of Th-MOF was further examined in binary/ternary mixed solution (MO + MB, MO + Rhb, MO + MB + alizarin and MO + Rhb + alizarin) containing dyes with different charges (Figure 7). Interestingly, the removal of both the linear and triangular cationic dye molecules by Th-MOF in the mixed dye solution is enhanced compared to the single dye solution, especially cationic dyes (Figure 8). We deem that due to the large aperture characteristics of MOF Th-TATAB, dye molecules with different charges co-existing in solution may undergo a co-adsorption process.[51] It is because of this co-adsorption process that MOF Th-TATAB exhibits mutual enhancement of adsorption capacity toward anions, neutral and cations dye molecules in the mixed solution.[51] From the above adsorption study, it can be concluded that Th-TATAB might be the better candidate for simultaneous removal of anionic, neutral and cationic dyes.

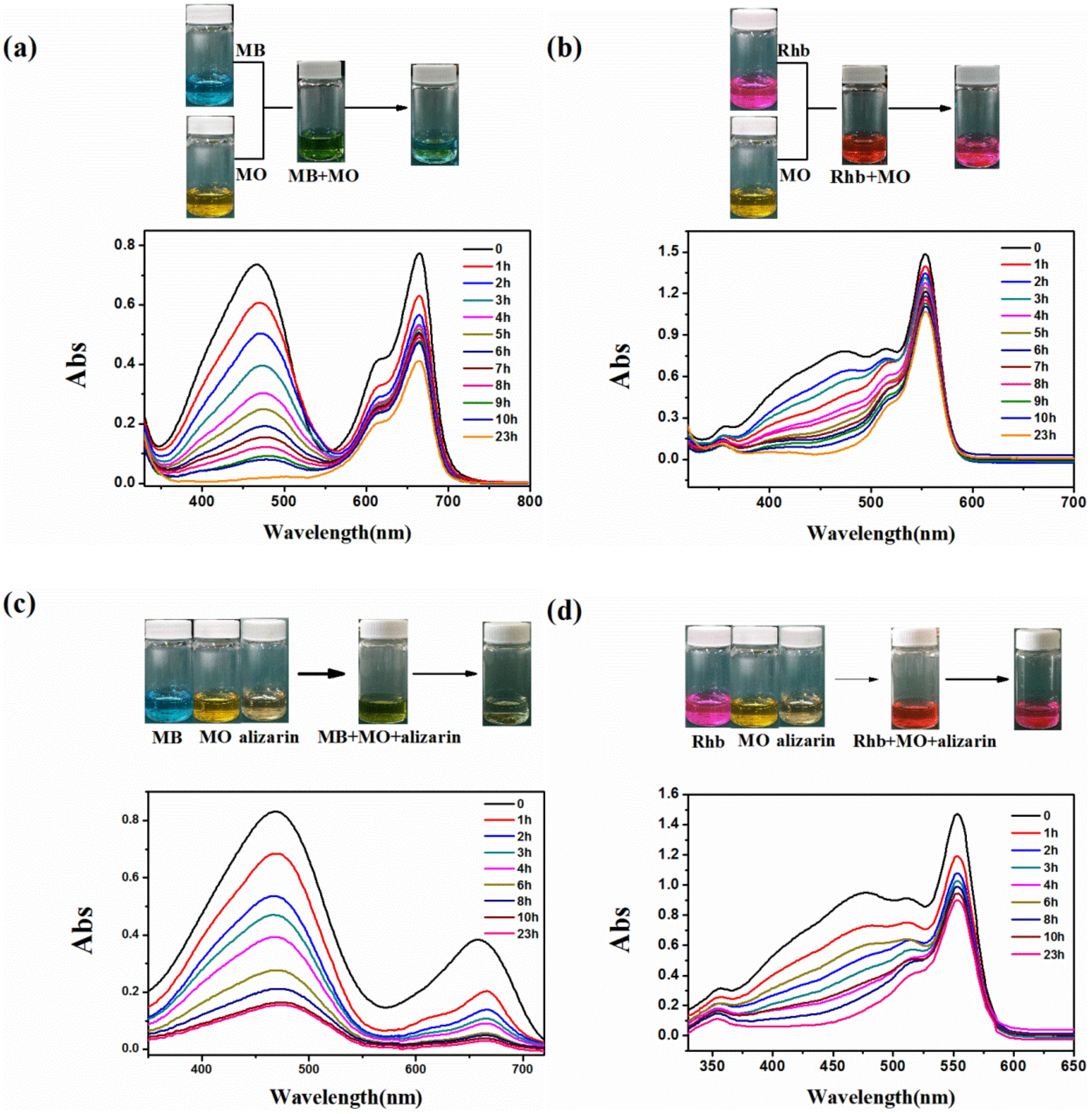


Fig 7. UV-visible absorption spectrum of the solution containing mixed dyes. (a) MO and MB; (b) MO and Rhb; (c) MO, MB and alizarin; (d) MO, Rhb and alizarin. The insets show the change in color of the mixed dye solution after adsorption.

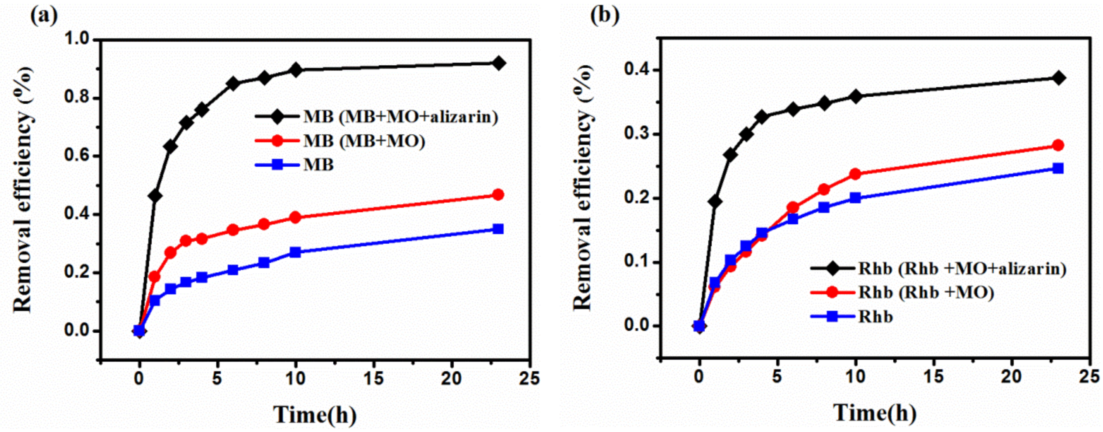


Fig 8. (a) Removal efficiency of MB in mixed solution (MB + MO + alizarin and MB + MO) and single dye solution; (b) Removal efficiency of RhB in mixed solution (Rhb +MO and Rhb + MO + alizarin) single dye solution.

It is necessary to pointed out that, a large number of dye release experiments have been carried out to study the desorption behavior of dyes, but no desorption behavior has been observed. We infer that, similar to the incomplete desorption of iodine, the unique host-guest interaction may facilitate the adsorption of the dye, but weaken dye desorption from dye-loaded samples. In particular, the double-layered π-electron walls formed by TATAB ligands may also hinder the dye release behavior.

In summary, a novel thorium-based MOF Th-TATAB with unique double-walled tetrahedral cage structure was designed and synthesized by self-assembly method, and its adsorption performance towards iodine and dye was investigated. The Th-MOF displays excellent adsorption properties towards iodine in cyclohexane solution. Moreover, anionic, neutral and cationic dye molecules can be adsorbed by this MOF from aqueous solution to some extent, in which linear dye molecules are better adsorbed. In particular, anions, neutral and cations dyes can be removed simultaneously in the mixed solution, and the adsorption capacity is mutually enhanced. The experimental results demonstrate that MOF Th-TATAB is a good potential candidate for adsorption of iodine and dye pollutants, which provides a new strategic idea for exploiting the physical and chemical properties and practical application of Th-MOF. In addition, it is very meaningful to explore the adsorption performance of MOF on iodine under humidity conditions, so we intend to conduct this research in the next step.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental and characterization data (PDF)

Supporting Figures S1-S17□ (PDF)

Crystallographic data (CCDC No.1871747) (CIF)

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ACKNOWLEDGMENT

This work was supported by the grants of the National Natural Science Foundation of China (No. 21571091) and Commonweal Research Foundation of Liaoning province in China (No. 20170055) for financial assistance.

ABBREVIATIONS

Th-TATAB, $Th_6O_4(OH)_4(H_2O)_6(TATAB)_2(HCO_2)_6$; MB, methylene blue ; MO,methyl orange; Rhb, rhodamine B.

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For Table of Contents Use Only

A Double-walled Thorium-based Metal-Organic Framework (MOF) as a Promising Dual Functional Absorbent for Efficiently Capturing Iodine and Dyes

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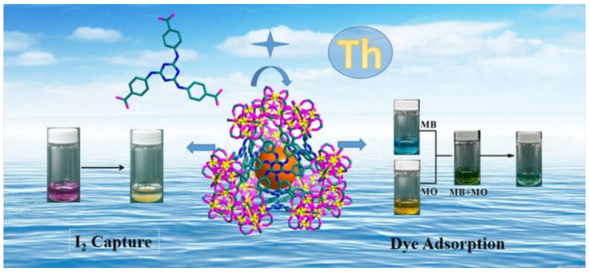
TOC



Synopsis

A novel thorium-based MOF Th-TATAB with rare double-walled tetrahedral cage structure. The thorium-based MOF can be used as an promising dual functional adsorbent for iodine capture in cyclohexane solution and the adsorptive removal of dye contaminants in aqueous solution, whcich provided a new strategic idea for opening up the potential applications of thorium-based MOF and understanding actinides chemistry.