

· 研究论文 ·

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## 二维 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的合成及吸附去除水中甲基橙的研究\*

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**摘要:** 多孔配位聚合物因结构可调, 比表面积大, 选择性、稳定性及可重复性优异, 作为吸附剂在去除废水染料方面引起了研究人员的广泛关注。利用柔性间苯二乙酸 (mpda)、刚性三咪唑苯 (tib) 合成配位聚合物 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 。在 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的结构中, tib配体作为三节点与Ni(II)离子配位形成2D网格面, 顺式mpda以端基式附着在2D网格面上, 再通过mpda的未配位羧基O与配位水分子之间O—H...O相互作用(OO...O3 0.2624 nm,  $\angle\text{O5—H5A...O2}=155.41^\circ$ )形成三维超分子网络结构。同时对 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的热稳定性、相纯度和比表面积进行了检测, 发现晶体基本骨架在316 °C以下稳定, 晶体材料相纯度高, 比表面积和平均孔径分别为58 m<sup>2</sup>/g、15.47 nm, 可作为稳定的吸附剂。在水体系中利用 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 对甲基橙染料进行吸附去除, 吸附量为18.64 mg/g。吸附数据与Langmuir模型和拟二级动力学方程具有更高的拟合程度, 以此可判断吸附过程为单层化学吸附; 当pH=4时, 吸附阴离子型染料-甲基橙量最大, 并且 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 表面的 $\zeta$ 电位说明其表面呈正电荷, 故此吸附作用力主要为静电相互作用; 热力学研究说明该吸附是自发的放热熵减过程。

**关键词:** 配位聚合物, 晶体结构, 热稳定性, 染料, 吸附性能

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### 1 前言

染料可分为合成染料和天然染料。天然染料环保, 但易褪色、稳定性差, 故在造纸、纺织、食品、化妆品和皮革等工业中较少使用。在这些工业中首选合成染料, 因为其稳定性好, 颜色种类多<sup>[1,2]</sup>。常用的合成染料有甲基橙(MO)、碱性品红(BF)、亚甲基蓝(MB)、孔雀石绿(MG)、亮绿(BG)、刚果红(CR)、尼罗蓝(NB)、结晶紫(CV)、碱性蓝(B41)、蓝色

B(AB)、金胺O(AO)、碱性红(B46)、罗丹明B(RhB)等<sup>[3,4]</sup>。合成染料在水中具有较高的光稳定性、热稳定性和化学稳定性<sup>[5]</sup>, 会增加水域的生化需氧量(Biochemical Oxygen Demand, BOD)和化学需氧量(Chemical Oxygen Demand, COD)<sup>[6]</sup>。水中氧量的减少会影响水生植物的光合作用, 破坏生态系统的平衡和完整性<sup>[7-10]</sup>, 因此合成染料废水的处理已成为全球关注的问题。

目前, 吸附、高级氧化、膜分离、电解、

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催化还原、光催化等方法已广泛应用于染料去除<sup>[11]</sup>。其中, 吸附技术因其效率高、成本低、有害副产品少、能耗低而被认为是最有前途的环境修复技术<sup>[12]</sup>。良好的吸附剂应具有多孔和比表面积大的特点, 以快速有效地吸附<sup>[13-14]</sup>。常用的吸附剂有活性炭、沸石和聚合物等多孔材料, 但这些多孔材料具有对染料去除能力低、接触时间长、成本高等缺点<sup>[15]</sup>。金属有机框架(Metal-Organic Frameworks, MOFs)材料表现出吸附能力强、热稳定性高、使用寿命长、材料多样性、孔径可调等优良性能, 是一种良好的吸附剂<sup>[16-19]</sup>。例如, Li等<sup>[20]</sup>制备了2种MOFs[MIL-53(Al)-NH<sub>2</sub>和MIL-53(Al)], 用于MG和MB的吸附去除; Xin等<sup>[21]</sup>合成了MnPc(G-Fe<sub>2</sub>O<sub>3</sub>/C), 用于去除MO染料; Chinthamreddy等<sup>[22]</sup>合成了Zn-BTC、Zn-BTC@PAA、Zn-BTC@PAA@CTAB共3种MOFs, 用于MB、MO、CR的吸附去除。

与刚性苯二甲酸相比, 柔性苯二乙酸有多种配位模式, 使MOFs晶体材料具有丰富多样的结构。刚性均苯三咪唑大分子配体, 其大分子长骨架易形成孔洞结构, 利于增大MOFs的比表面积, 提高吸附效率。目前利用这2类配体合成了11种MOFs晶体材料<sup>[23-26]</sup>, 但没有进一步研究其吸附去除染料的性能。

基于上述考虑, 本课题组利用间苯二乙酸、1,3,5-三(1-咪唑基)苯和硝酸镍合成了新的配位聚合物晶体材料[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O, 并对其结构、稳定性、比表面积进行了研究。同时研究了该配位聚合物对合成染料甲基橙的吸附等温线、动力学和热力学吸附参数。结果表明, pH值、初始染料浓度、MOFs表面性能、温度等参数对其吸附能力均有影响。该研究为再生清洁能源提供了一种新的吸附剂, 其在水环境保护中具有广阔的应用前景。

## 2 实验部分

### 2.1 仪器和试剂

仪器: Flash 2000型有机元素分析仪; BrukerD8型X-射线衍射仪(Cu-K<sub>α</sub>辐射, λ=0.15418 nm); Bruker Smart 1000 CCD型单晶衍射仪(Mo-K<sub>α</sub>辐射, λ=0.071073 nm); TA Q550型热重分析仪; IRAFFINITY-1S FT-IR型光谱仪; ASAP 2460 3.01型比表面积仪; UV-2550型分光

光度计; Malvern Zetasizer Nano ZS90型分析仪; THZ-82A型水浴恒温振荡器。

试剂: Ni(Ac)<sub>2</sub>·4H<sub>2</sub>O、均苯三咪唑、对苯二乙酸、醋酸钠, 均为分析纯。

### 2.2 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的合成

将Ni(Ac)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 219.7 mg)、均苯三咪唑 (0.1 mmol, 276.3 mg)、邻苯二乙酸 (0.1 mmol, 194.2 mg)、醋酸钠缓冲液 (3 mL, pH=5) 和异丙醇 (1 mL) 混于20 mL玻璃瓶内, 超声30 min后置于温度为95 °C的烘箱中反应72 h, 冷却至室温得到绿色块状晶体。C<sub>25</sub>H<sub>26</sub>NiN<sub>6</sub>O<sub>7</sub>计算值(%): C 51.66, H 4.51, N 14.46; 实验值(%): C 51.85, H 4.73, N 14.61。

### 2.3 染料溶液的制备

使用超纯水作为溶剂, 将固体的MO、BF、RhB和MB配制成浓度为20 mg/L的溶液。通过紫外可见分光光度计测得溶液分别在463 nm (MO)、552 nm (RhB)、543 nm (BF)和664 nm (MB)处出现吸光度。通过配制不同浓度的MO溶液(5~40 mg/L), 得到关于MO的标准曲线。由式(1)<sup>[27]</sup>计算[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O对染料的平衡吸附量 $q_e$ 。

$$q_e = (C_0 - C_e)V/m \quad (1)$$

式中:  $C_0$ 与 $C_e$ 分别为染料溶液的初始浓度与平衡浓度, mg/L;  $V$ 为染料溶液的总容积, L;  $m$ 为吸附剂的质量, g。

利用时间间歇法测量24 h内[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O吸附染料的动力学过程, 时间间隔为5、10、20、30、60、90、120、180、300、600和1440 min。采用浓度为5~40 mg/L的染料溶液进行24 h吸附等温线实验, 使用紫外可见光谱法实时监测染料浓度的变化。吸附剂均使用0.22 μm滤芯过滤。

## 3 结果与讨论

### 3.1 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的结构

单晶X衍射分析显示, 该配位聚合物晶体属于三斜晶系、P<sub>1</sub>空间群,  $a=8.292(2)$  nm,  $b=9.680(2)$  nm,  $c=16.467(4)$  nm,  $\alpha=89.753(4)^\circ$ ,  $\beta=88.369(4)^\circ$ ,  $\gamma=73.674(4)^\circ$ ,  $V=1267.9(5)$  nm<sup>3</sup>,  $Z=2$ 。[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的不对称单元由1个Ni(II)离子、1个mpda配体、1个tib配体、3个水分子组成。其不对称单元包含2个晶

体学上独立的Ni(II)中心,每个中心都有1个不同的配位模式。Ni1中心离子具有扭曲的八面体配位,2个氮原子由2个不同的tib配体提供,2个氧原子来自1个mpda配体,另2个氧原子来自2个水分子。Ni2中心原子也具有扭曲的八面体配位,4个氮原子由4个不同的tib配体提供,2个氧原子来自2个不同的mpda[图1(a)]。在 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 结构中,均苯三咪

唑作为三节点与Ni(II)离子配位形成2D网格面[图1(b)];顺式mpda有2个羧基均去质子,但只有1个进行单齿配位,故该配位模式的mpda配体只能以端基式附着在上述2D网格面上[图1(b)];再通过mpda的未配位羧基O与配位水分子之间 $\text{O}-\text{H} \cdots \text{O}$ 相互作用( $\text{O}0 \cdots \text{O}3$  0.2624 nm,  $\angle \text{O}5-\text{H}5\text{A} \cdots \text{O}2=155.41^\circ$ )形成三维超分子网络结构[图1(c)]。

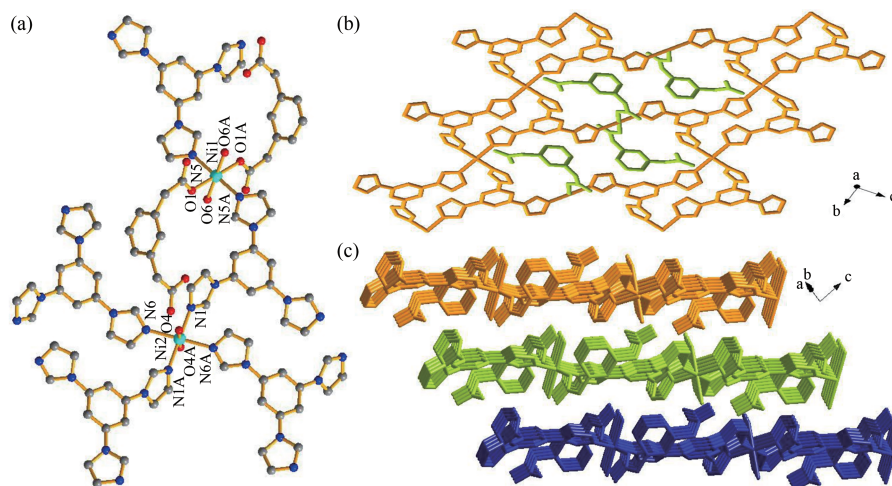


图1  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的晶体结构图:(a) Ni(II)的配位环境;(b)均苯三咪唑与Ni(II)构成二维网格面;(c)二维面堆积形成三维超分子结构。

Figure 1 Crystal structure of  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ : (a) The coordination environment of Ni(II); (b) Pyrenetriazole and Ni(II) form a two-dimensional mesh surface; (c) Two dimensional stacking forms a three-dimensional supramolecular structure.

### 3.2 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的FT-IR、热重、PXRD、BET分析

$[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的红外光谱如图2所示,3600~3200  $\text{cm}^{-1}$ 处的特征峰属于水分子O—H基团的伸缩振动<sup>[28]</sup>;1700~1500  $\text{cm}^{-1}$ 处的特征峰属于羧酸官能团COO<sup>-</sup>的对称以及不对称伸缩振动<sup>[29]</sup>;1356  $\text{cm}^{-1}$ 处的特征峰属于咪唑环C—N键的伸缩振动<sup>[30]</sup>。这些特征峰与晶体结构分析相一致。

在空气气氛条件下,采用热分析仪以10  $^\circ\text{C}/\text{min}$ 的升温速率测得 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的热失重曲线,结果如图3所示。在室温600  $^\circ\text{C}$ 范围内, $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的失重过程分2步完成,由图3可见配位聚合物对应的配位水分子和结晶水分子逐渐释出,在95~125  $^\circ\text{C}$ 时重量下降8.7% (计算值均为9.3%)。配位聚合物的基本骨架在316  $^\circ\text{C}$ 以下是稳定的,随着温度升高,配体mpda、tib逐渐失去。当温度加热至500  $^\circ\text{C}$

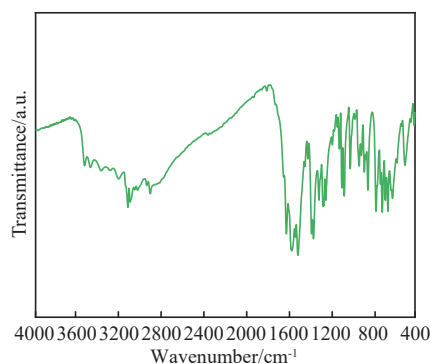


图2  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的红外光谱。

Figure 2 IR spectrum of  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ .

时其被氧化为NiO,此时产物剩余13.89% (计算值均为12.85%)。

为了确定材料的相纯度,在室温下测试 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 的粉末X射线衍射(PXRD),实验测试条件为电压40 kV,电流30 mA,扫描范围为5~60 $^\circ$ 。如图4所示,实验PXRD和单晶结构模拟的峰位置一致,证明其相

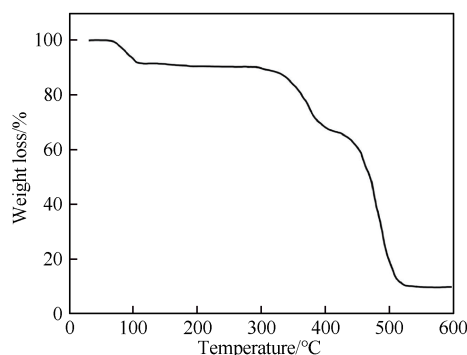


图3 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的热重曲线.  
Figure 3 Thermogravimetric curve of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O.

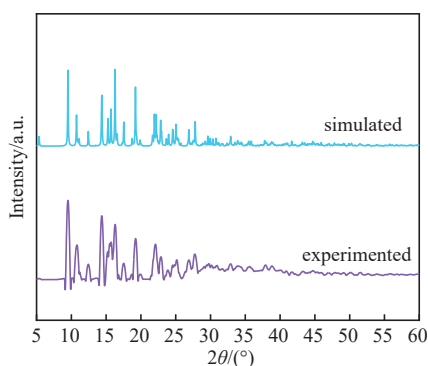


图4 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的PXRD.  
Figure 4 PXRD of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O.

纯度较好, 一些衍射峰强度的差异可能归因于晶体与粉末样品的取向区别。

通过 BET 测试, 结果表明 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 的比表面积为 58 m<sup>2</sup>/g。77 K 下 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 对 N<sub>2</sub> 吸附-脱附的行为如图 5 所示, 该等温线属于 II 型等温线。采用 Barret-

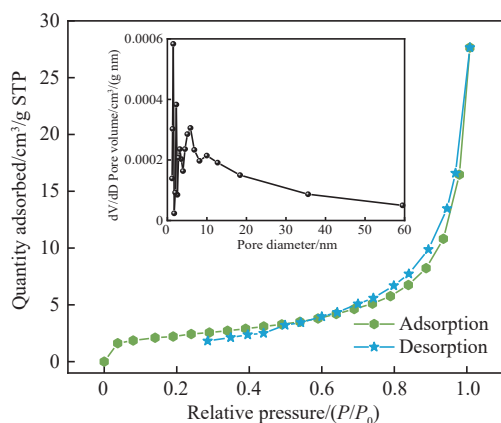


图5 77 K 下 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 的 N<sub>2</sub> 吸附-脱附等温线(插图:孔径分布).

Figure 5 N<sub>2</sub> adsorption-desorption isotherms of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O at 77K (inset: pore size distribution).

Joyner-Halenda (BJH) 方法进行孔径分布分析, 从图 5 中可以看到 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 属于介孔材料, 平均孔径为 15.47 nm。

### 3.3 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 吸附水中甲基橙性能测试

#### 3.3.1 染料的选择性

将 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 作为吸附剂对不同染料 (MB、BF、RhB、MO) 进行选择测试。4 种染料溶液 (20 mL, 20 mg/L) 中均加入 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (5 mg), 利用紫外可见光谱测定 24 h 后染料浓度的变化, 结果如图 6 所示。从图 6 可以看出, [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 对 4 种染料的吸附量均不同, 利用式 (1) 换算出 4 种染料 MB、BF、RhB、MO 吸附量分别为 1.329、8.280、13.930、18.640 mg/g, 说明 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 对 MO 的选择性最好, 故研究了 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 对 MO 的吸附行为。

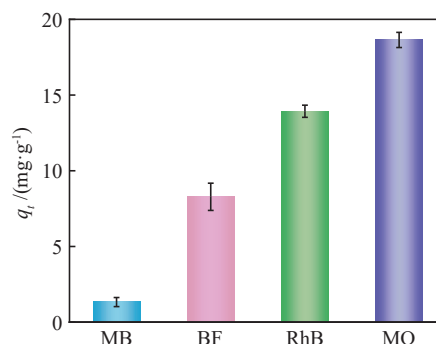


图6 水中染料吸附选择图 ( $T=298$  K,  $C_0=20$  mg/L).

Figure 6 Dye adsorption selection plot in water ( $T=298$  K,  $C_0=20$  mg/L).

#### 3.3.2 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 吸附动力学

从图 7 可以看出, [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O 对 MO 的吸附量随时间的延长而逐渐增加, 当时间达到 1440 min 时, 吸附量逐渐趋于平移, 说明此时吸附达到饱和状态, 吸附量为 18.64 mg/g。

为了探究其吸附机理及速度控制步骤, 利用伪一阶动力学模型、伪二阶动力学模型、粒子内扩散模型<sup>[31-33]</sup>对其动力学数据进行拟合, 如式 (2)~(4) 所示。

$$\text{伪一阶动力学模型: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\text{伪二阶动力学模型: } t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

$$\text{粒子内扩散模型: } q_t = k_{di} t^{1/2} + C_i \quad (4)$$

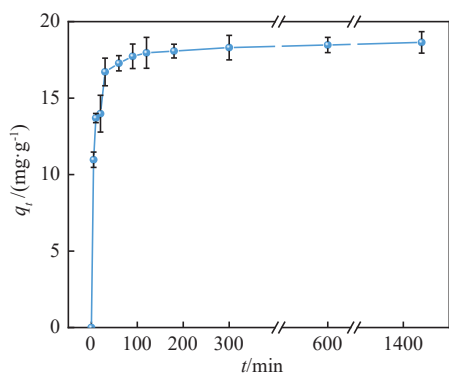


图7 时间与吸附量关系图 ( $T = 298\text{ K}$ ,  $C_{\text{MO}} = 20\text{ mg/L}$ ).

Figure 7 Plot of time versus adsorption capacity ( $T = 298\text{ K}$ ,  $C_{\text{MO}} = 20\text{ mg/L}$ ).

式中： $q_e$ 与 $q_t$ 分别为平衡时和 $t$ 时[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O对MO的吸附量， $k_1$ 、 $k_2$ 为吸附速率常数， $k_{\text{di}}$ 为扩散速率常数， $C_i$ 为截距。

3个动力学模型参数见表1，式(2)、(3)的

表1 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O吸附MO动力学模型参数。

Table 1 Kinetic parameters of MO adsorption by [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O.

Kinetic Models	Parameters			
Pseudo-first-order kinetic	$q_{e, \text{exp}}/(\text{mg}\cdot\text{g}^{-1})$ 18.64	$q_{e, \text{cal}}/(\text{mg}\cdot\text{g}^{-1})$ 3.667	$k_1/(\text{min}^{-1})$ 0.00644	$R^2$ 0.626
Pseudo-second-order kinetic	$q_{e, \text{exp}}/(\text{mg}\cdot\text{g}^{-1})$ 18.64	$q_{e, \text{cal}}/(\text{mg}\cdot\text{g}^{-1})$ 18.62	$k_2/(\text{g}\cdot\text{min}^{-1}\cdot\text{mg}^{-1})$ 0.0119	$R^2$ 0.999
Intra-particle diffusion model	$k_{\text{id}}/(\text{mg}\cdot\text{min}^{-1}\cdot\text{mg}^{-1/2})$	$C/(\text{mg}\cdot\text{g}^{-1})$		$R^2$
Step 1	1.34	7.027		0.749
Step 2	0.319	14.24		0.999
Step 3	0.0278	17.60		0.996

### 3.3.3 [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O吸附等温线

配制浓度为5~40 mg/L的系列MO溶液，测试[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O对MO的吸附量与浓度的关系(图8)，再利用式(5)~(7)<sup>[37-39]</sup>探讨[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O对MO的吸附等温线。

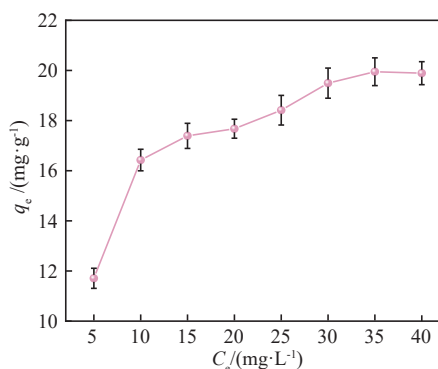


图8 MO初始浓度与吸附量的关系图 ( $T = 298\text{ K}$ ,  $C_{\text{MO}} = 5\sim 40\text{ mg/L}$ ).

Figure 8 Plot of MO initial concentration versus adsorption capacity ( $T = 298\text{ K}$ ,  $C_{\text{MO}} = 5\sim 40\text{ mg/L}$ ).

$R^2$ 分别为0.999、0.626，并且式(2)中平衡吸附量的计算值与实验值更接近，说明伪二阶动力学模型可以更好地描述吸附过程。因此，该吸附过程可能是化学吸附<sup>[34]</sup>。通过粒子内扩散模型可以看出， $k_1 > k_2 > k_3$ ，这是由于MO染料溶液与[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的浓度差较大，第1步[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的吸附速率较快；第2步MO逐渐从[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O外表面进入孔道内部，由于孔道内部存在空间内阻，导致速率 $k_2 < k_1$ ；第3步MO逐步填满[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的孔道内部，[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的活性位点降低，粒子内扩散减慢，达到吸附平衡<sup>[35]</sup>。另外，这3步均没有经过坐标原点，说明粒子内扩散参与了吸附的过程，但不是唯一的速度控制步骤，而是粒子外扩散和粒子内扩散同时发生<sup>[36]</sup>。

$$\text{Langmuir: } q_e = q_m K_L C_e / (1 + K_L C_e) \quad (5)$$

$$\text{Freundlich: } q_e = K_F C_e^{1/n} \quad (6)$$

$$\text{Temkin: } q_e = RT \ln(K_T C_e) / b \quad (7)$$

式中： $q_m$ 与 $q_e$ 分别为[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的最大和平衡时的吸附量， $C_e$ 为平衡时MO的浓度， $K_L$ 、 $K_F$ 、 $K_T$ 分别为Langmuir、Freundlich和Temkin常数， $n$ 为Freundlich参数， $b$ 为吸附热常数， $R$ 为气体常数， $T$ 为吸附温度。

图8可见，[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O的吸附量随着MO溶液初始浓度的增加而增大。这可能是由于MO溶液初始浓度越大，浓度梯度驱动力越大，MO分子与[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O之间发生更多有效碰撞。

利用式(5)~(7)对等温线数据进行拟合得到图9和表2，Langmuir、Freundlich、Temkin模型的 $R^2$ 分别为0.966(更接近于1)、0.898、0.930，且Langmuir拟合曲线计算得到的最大吸附量与

实验值相近。因此, Langmuir 模型与吸附等温线拟合程度较好, 该吸附过程主要是单层吸附。

通过无量纲恒定分离因子 ( $R_L$ ) 进一步判断 MO 与  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  之间的亲和力。 $R_L$  的计算方程为式 (8)。

$$R_L = 1 / (1 + K_L C_0) \quad (8)$$

当  $0 < R_L < 1$ , 说明吸附过程是有利的, 当  $R_L > 1$ , 吸附过程是不利的<sup>[40]</sup>。本研究中  $0 < R_L < 1$ , 因此  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  吸附 MO 的过程良好。

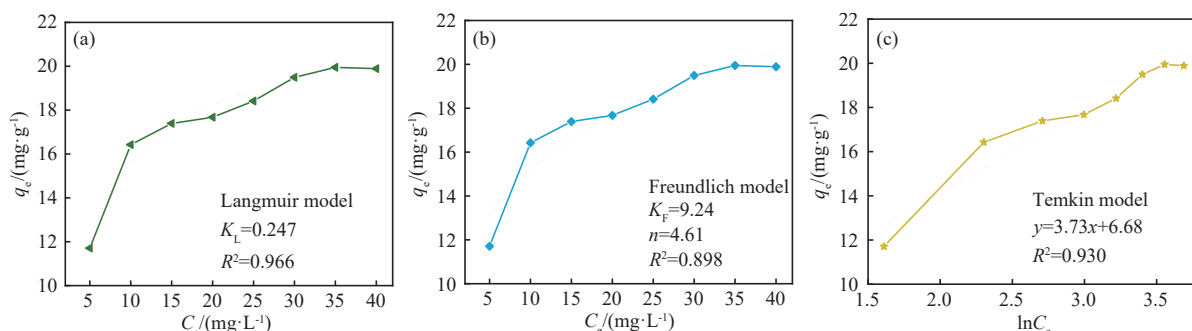


图9 (a) Langmuir 模型; (b) Freundlich 模型; (c) Temkin 模型 ( $T = 298\text{K}$ ,  $C_{\text{MO}} = 5 \sim 40 \text{mg/L}$ )。

Figure 9 (a) Langmuir model; (b) Freundlich model; (c) Temkin model ( $T = 298\text{K}$ ,  $C_{\text{MO}} = 5 \sim 40 \text{mg/L}$ )。

表2  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  吸附 MO 等温线模型参数。

Table 2 Isotherm parameters of MO adsorption by  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ .

Models	Parameters									
Langmuir isotherm	$q_{\text{m,exp}} (\text{mg} \cdot \text{g}^{-1})$	19.85	$q_{\text{m,cal}} (\text{mg} \cdot \text{g}^{-1})$	21.93	$K_L (\text{L} \cdot \text{mg}^{-1})$	0.247	$R_L$	0~1	$R^2$	0.996
Freundlich isotherm	$n$	4.16	$K_F [(\text{L}/\text{mg})^{1/n}]$	9.24					$R^2$	0.898
Temkin isotherm	$b$	665	$K_T (\text{L} \cdot \text{mg}^{-1})$	6.01					$R^2$	0.930

### 3.3.4 $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ 吸附热力学

吸附热力学对于研究  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  吸附 MO 的机理具有重要意义。在 298、308、318 K 下测试  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  对 MO 的吸附实验 (图 10)。同时利用式 (9)~(11) 计算吉布斯自由能 ( $\Delta G$ )、焓变 ( $\Delta H$ )、熵变 ( $\Delta S$ )<sup>[41-43]</sup>, 结果见表 3。

$$K_d = q_e / c_e \quad (9)$$

$$\ln K_d = \Delta S / R - \Delta H / RT \quad (10)$$

$$\Delta G = \Delta H - T \Delta S \quad (11)$$

式中:  $K_d$  为热力学平衡常数,  $R$  为气体常数,  $T$  为吸附温度。

从图 10 可以看出, 随着温度的升高最大吸附量逐渐变小; 从表 3 可以看出 3 个温度下  $\Delta H$ 、 $\Delta G$ 、 $\Delta S$  均为负数, 说明该吸附过程属于放热熵减的自发反应。

表3  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  吸附 MO 热力学参数。

Table 3 Thermodynamic parameters of MO adsorption by  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ .

$T$ (K)	$\Delta G / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
298	-0.7371	-9.254	-28.58
308	-0.4514	-9.254	-28.58
318	-0.1656	-9.254	-28.58

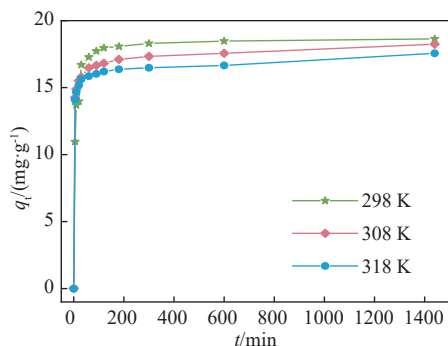


图10  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  在不同温度下的动力学吸附过程 ( $C_{\text{MO}} = 20 \text{mg/L}$ )。

Figure 10 Adsorption process of  $[\text{Ni}(\text{tib})(\text{mpda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  at different temperatures ( $C_{\text{MO}} = 20 \text{mg/L}$ )。

### 3.3.5 离子强度的影响

将不同浓度的 NaCl (5~30 g/L) 加入 MO 溶液中, 得到 MO 吸附量与 NaCl 浓度的变化图

(图 11)。可以看出[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O对MO的吸附量随着NaCl浓度的增加而减少,这是由于NaCl浓度的增加,使得基质效应扩大和

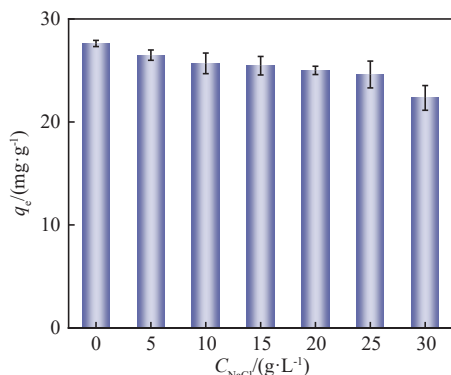
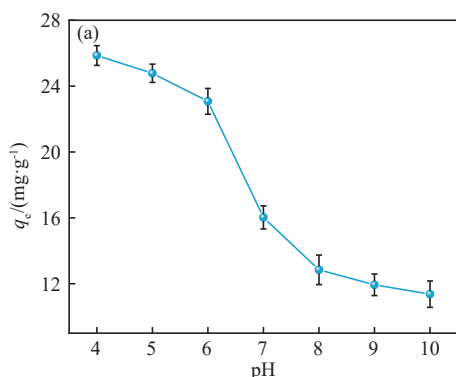


图 11 离子强度对吸附量的影响( $T=298$  K,  $C_{NaCl}=5\sim 30$  g/L,  $C_{MO}=20$  mg/L).

Figure 11 Effects of ionic strength on adsorption capacity ( $T=298$  K,  $C_{NaCl}=5\sim 30$  g/L,  $C_{MO}=20$  mg/L).



溶液黏度<sup>[44]</sup>增加,进而对整个吸附的传输过程和扩散过程都有不利影响,并且在NaCl逐渐占据[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的孔隙后,[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的活性位点会减少,导致吸附量逐渐降低。

### 3.3.6 吸附机理

pH值对吸附过程有显著的影响,故在不同pH下探究了[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O对MO的吸附性能。从图12可以看出,当pH=4时,MO的吸附量最大,随着pH增大吸附量减小。根据静电相互作用可以解释该过程<sup>[45]</sup>。通过测试[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O表面的 $\zeta$ 电位,发现pH=4时,[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O表面呈现正电荷;pH=5~9时,[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O表面呈现负电荷。MO为阴离子型染料,说明MO溶液与[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O之间存在静电斥力,导致吸附量逐渐变小。

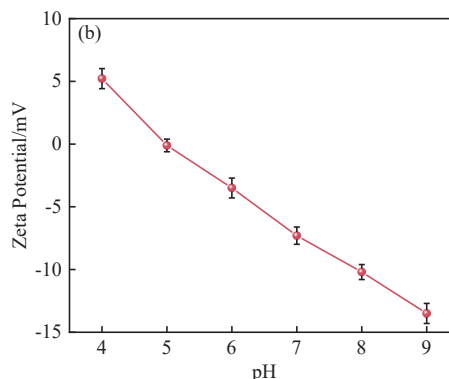


图 12 (a) [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的吸附量与pH值的关系; (b) [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O的 $\zeta$ 电位.

Figure 12 (a) Plot of adsorption capacity of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O versus pH; (b)  $\zeta$ -potential of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O.

## 4 结论

(1) 本文利用水热法合成了配位聚合物[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O。晶体结构解析表明:tib与中心Ni(II)形成波浪二维面,顺式mpda只有1个羧基与中心Ni(II)配位,附着在二维面上,相邻面的mpda未配位羧基与结晶水具有氢键作用力,从而构成复杂的三维超分子结构。

(2) [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O性能表征表

明:基本骨架在316℃时开始分解塌陷,晶体纯相比表面积为58 mg/g、平均孔径为15.47 nm。

(3) 在水体系中利用[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O对甲基橙染料进行吸附去除,吸附量为18.64 mg/g。主要的吸附去除机制为静电相互作用。

(4) 该项研究为构建吸附性能配位聚合物提供了可行的思路,并促进了[Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O在吸附去除染料方面的应用,对生态环境的保护具有重要意义。

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Research paper

## Study on the Synthesis of 2D [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O and Its Adsorption to Remove Methyl Orange in Water

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**Abstract** Porous coordination polymers have attracted significant attention due to their tunable structure, large specific surface area, excellent selectivity, stability and reproducibility, making them ideal adsorbents for removing dyes from wastewater. In this paper, a coordination polymer called [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O was synthesized using flexible m-phenyldiacetic acid (mpda) and rigid 1,3,5-tris (1-imidazolyl) benzene (tib). In [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O, the tib acts as a trinode coordinating to the Ni(II) ion, forming a 2D lattice surface. The cis-mpda is attached to the 2D lattice surface in a telomeric fashion. The uncoordinated carboxylate group O of the mpda forms a 3D supramolecular network structure through O—H···O interactions with a coordinating water molecule (O0···O3 0.2624 nm, ∠O5—H5A···O2=155.41°). The thermal stability, phase purity, and specific surface area of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O were also examined in the study. It was found that the polymer's skeleton begins to decompose and collapse at 316°C. The highly pure crystalline material had a specific surface area of 58 m<sup>2</sup>/g and average pore size of 15.47 nm. The [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O was shown to effectively remove methyl orange dye in an aqueous system, with an adsorption capacity of 18.64 mg/g. The adsorption data are fitted well with the Langmuir model and the proposed second-order kinetic equation, indicating that the adsorption process is a monolayer chemisorption. The adsorption of anionic dye-methyl orange is the largest at pH=4, and the ζ potential of [Ni(tib)(mpda)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O indicates that the surface has positive charges, validating the adsorption force mainly from electrostatic interaction. Moreover, thermodynamic studies reveal that the adsorption process is spontaneous and exothermic, and results in entropy reduction.

**Keywords** Coordination polymer, Crystal structure, Thermal stability, Dye, Adsorption performance

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