

N/MOF(Fe)的制备及 Cr^{6+} 原位吸附-还原行为

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摘 要: 含 Cr^{6+} 废水引起的环境污染问题备受关注, 金属有机框架(MOF)得益于其大比表面积和高孔隙率, 已广泛应用于吸附 Cr^{6+} 。通过溶剂热法合成了尿素改性的 N/MOF(Fe), 研究了制备条件对 Cr^{6+} 的吸附性能的影响, 并对 N/MOF(Fe)进行结构表征和性能分析。结果表明: 与 MOF(Fe)相比, N/MOF(Fe)孔径和孔容增大, 吸附能力和吸附速率均有提升。考察了吸附实验条件对 N/MOF(Fe) 吸附性能的影响, 在 Cr^{6+} 初始浓度为 5 mg/L, N/MOF(Fe)投加量为 0.8 g/L, pH 值为 5.6, 反应时间为 40 min 时, 吸附率可达 95.23%。建立了 N/MOF(Fe)吸附 Cr^{6+} 的吸附动力学和热力学方程。结果表明: 吸附过程符合二级反应动力学方程和 Langmuir 吸附等温模型, 吸附反应是一个自发放热过程。通过自由基捕获实验, 验证了 $\cdot\text{O}_2^-$ 的存在, 根据 XPS 分析, 证实了 Cr^{6+} 被 $\cdot\text{O}_2^-$ 还原为 Cr^{3+} , 提出了 N/MOF(Fe)吸附 Cr^{6+} 的原位吸附-还原联合作用机制。

关键词: 金属有机框架; 六价铬; 吸附; 尿素

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铬广泛应用于电镀、冶金、纺织等工业领域^[1], 由此造成的六价铬(Cr^{6+})水环境污染问题也日益严重^[2]。 Cr^{6+} 被列为I类致癌物, 进入人体后患癌症、呼吸道疾病的风险将大大提高, 对人体产生极强的危害^[3]。

Cr^{6+} 的去除方法多种多样, 如化学沉淀、高级氧化和吸附等^[4], 其中吸附法由于操作简便、成本低廉等优点引起了研究人员们的注意^[5]。金属有机框架(MOF)是由有机配体与金属离子连接而成的多孔材料^[6], 具备比表面积大、可调控性强、孔隙率高等优势^[7], 已在吸附^[8]、催化^[9]、药物^[10]、传感器^[11]等领域广泛应用。研究表明, 杂化后 MOF 的吸附点位增加, 能量排布更加规则, 反应活性进一步提升^[12]。尿素是一种常见的结构剂, Seo 等^[13]制备的尿素-MIL-101 对甲硝唑的吸附性能比其他文献所报道的都要高, Ebrahim 等^[14]利用尿素引入 $-\text{NH}_2$ 基团增强了对 NO_2 的吸附, Figueroa-Quintero 等^[15]使用尿素作为结构剂制备的材料具有疏水性, 并且对甲苯、环己烷和间二甲苯均具备良好的吸附性能。

以邻苯二甲酸氢钾(KHP)作为有机配体合成 MOF 的相关研究很少, 在制备 MOF 常用的过渡金属离子中, 铁离子更绿色安全、易制取, 因此以铁盐制备 MOF。基于此, 本工作通过溶剂热法一步制备了尿素掺杂的 N/MOF(Fe), 研究了吸附反应及相关机制, 为含 Cr^{6+} 废水的处理以及 MOF 的制备和应用提供理论支持。

1 实验

1.1 试剂与仪器

主要试剂: 硫酸、乙酸、盐酸、乙醇、尿素、重铬酸钾、九水硝酸铁($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)、N, N-二甲基甲酰胺(DMF)、KHP, 以上试剂均为分析纯, 均购自国药集团; 二苯碳酰二肼购自天津瑞金特公司。

主要仪器: 紫外-可见分光光度计(L5S, 上海仪电分析仪器有限公司); 透射电子扫描显微镜(TEM, JEM2100F 日本电子); 扫描电子显微镜(SEM, Sigma500 德国蔡司); 能谱仪(EDS, xflash3160, 德国布鲁克); X 射线衍射仪(XRD,

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SmartLab, 日本理学); 比表面及孔径分析仪(SSA-4000, 北京彼奥德电子技术有限公司); X 射线光电子能谱(XPS, Escalab 250xi 赛默飞世尔科技公司)。

1.2 N/MOF(Fe)的制备

采用溶剂热法制备 N/MOF(Fe)材料。在 24 mL DMF 中加入 0.306 g KHP、1.212 g Fe(NO₃)₃·9H₂O 和 0.6 mL 乙酸, 搅拌溶解后将混合溶液转移到聚四氟乙烯内衬的反应釜中在 180 °C 反应 20 h, 通过离心分离得到红棕色沉淀, 分别用去离子水和乙醇洗涤数次, 最后在 80 °C 干燥过夜, 获得的材料命名为 MOF(Fe)。在混合溶液中加入 0.028 mol/L 尿素, 其余步骤与上述相同, 获得的材料命名为 N/MOF(Fe)。

1.3 N/MOF(Fe)吸附 Cr⁶⁺实验

取 5 mg/L Cr⁶⁺溶液 140 mL 置于烧杯中, 加入 0.2、0.4、0.6、0.8、1.0 g/L 吸附剂, 在 1、2、4、6、8、16、30、40 min 时取出适量溶液, 用滤膜过滤后

加入显色剂, 在 540 nm 处测量吸光度, Cr⁶⁺的去除率(C)和吸附容量(W)利用式(1)、式(2)计算。

$$C = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$W = \frac{(C_0 - C_t)V}{m} \times 100\% \quad (2)$$

其中: W 为吸附容量(mg, 每 1 g 吸附剂中); C_0 、 C_t 分别为初始和 t 时刻时 Cr⁶⁺浓度(mg/L); V 为溶液体积(mL); m 为吸附剂质量(g)。

2 结果与讨论

2.1 N/MOF(Fe)的制备

为了研究制备温度、制备时间、金属-配体摩尔比和 pH 值对材料吸附性能的影响程度以及最佳条件组合, 设计了 4 因素 3 水平的正交实验, 设计表及极差分析数据结果如下。

表 1 正交实验结果及数据分析表
Table 1 Orthogonal experiment results and data analysis table

Experiment No.	Preparation temperature (A)	Preparation time (B)	molar ratio of metal ions to organic ligands (C)	pH value (D)	Removal Efficiency of Cr ⁶⁺
1	160 °C	20 h	1.0:0.5	2.5	31.75%
2	160 °C	24 h	1.0:0.6	2.3	18.25%
3	160 °C	28 h	1.0:0.7	2.1	30.16%
4	180 °C	20 h	1.0:0.6	2.1	21.03%
5	180 °C	24 h	1.0:0.7	2.5	28.97%
6	180 °C	28 h	1.0:0.5	2.3	11.90%
7	200 °C	20 h	1.0:0.7	2.3	13.89%
8	200 °C	24 h	1.0:0.5	2.1	38.09%
9	200 °C	28 h	1.0:0.6	2.5	47.22%
K_1	0.802	0.667	0.817	1.079	
K_2	0.619	0.853	0.865	0.440	
K_3	0.992	0.893	0.730	0.893	
k_1	0.267	0.222	0.272	0.360	
k_2	0.206	0.284	0.288	0.147	
k_3	0.331	0.298	0.243	0.298	
Q	0.124	0.075	0.045	0.213	

K_1 , K_2 , K_3 are the corresponding level sums. k_1 , k_2 , k_3 are the corresponding level means. Q is range. Concentration of Cr⁶⁺ is 1 mg/L, and the dosage of MOF(Fe) is 0.5 g/L.

K_1 、 K_2 、 K_3 分别为对应的水平总和; k_1 、 k_2 、 k_3 分别为对应的水平均值; Q 为极差; Cr⁶⁺浓度为 1 mg/L, MOF(Fe)投加量为 0.5 g/L。极差值越大, 表明该因素的变化导致的实验结果波动越大, 极差从大到小排列为 $D>A>B>C$, 表明控制 pH 值对 MOF(Fe)吸附 Cr⁶⁺的效果最为重要。根据极差分析得出的最佳水平组合: $A_2B_1C_3D_2$, 即反应温度 180 °C、反应时间 20 h、金属与配体摩尔比 1.0:0.7、pH 值为 2.3。

在 MOF(Fe)的最佳制备条件基础上掺杂尿素合

成 N/MOF(Fe), 研究了尿素掺杂量对 N/MOF(Fe)吸附性能的影响。由图 1 可见, MOF(Fe)吸附率只有 50%左右, 而掺杂尿素后材料的吸附速率明显提高, 吸附性能显著提升, 这可能由孔径和孔容增大导致。

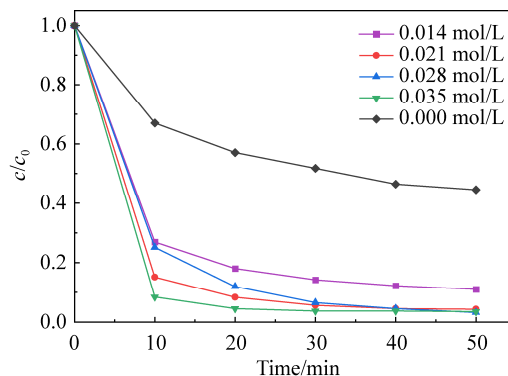
2.2 材料的表征

2.2.1 形貌结构表征 图 2 为 N/MOF(Fe)的 SEM 照片、TEM 照片、EDS 谱及 XPS 谱。由图 2a 可见, N/MOF(Fe)呈小球状。由图 2c~图 2d 可见, 材料主要由 C、N、O、Fe 等元素组成, 表明 N/MOF(Fe)合成比较成功。由图 2b 可见, N/MOF(Fe)的晶格条

纹较明显, 晶格间距为 0.12 nm, 对应于 Fe 的(721)晶面, 表明 N/MOF(Fe)中的 Fe 在合成过程中没有价态变化。

2.2.2 光谱表征 图 3 为 N/MOF(Fe)的 XRD 谱。由图 3 可见, N/MOF(Fe)的衍射峰较宽, 结晶度和衍射强度不高, 这可能是材料的结晶度低造成的, 与 Wang 等^[16]报道的情况类似。在 35.62°、40.78° 和 62.75° 出现了归属于 Fe₂O₃ 的特征峰, 表明铁离子是以 Fe³⁺ 的形式构建了 MOF 材料。

2.2.3 N₂ 吸附脱附等温线 掺杂尿素前后材料的 N₂ 吸附脱附等温线如图 4 所示。根据 IUPAC 分类, 表明 N/MOF(Fe)吸附符合 II 型等温线, 且出现了滞后环, 说明材料孔径主要属于介孔^[17], 相应的孔



Concentration of Cr⁶⁺ is 2 mg/L.

图 1 尿素掺杂量对 N/MOF(Fe)吸附性能的影响

Fig. 1 Effect of urea doping amount on N/MOF(Fe) adsorption performance

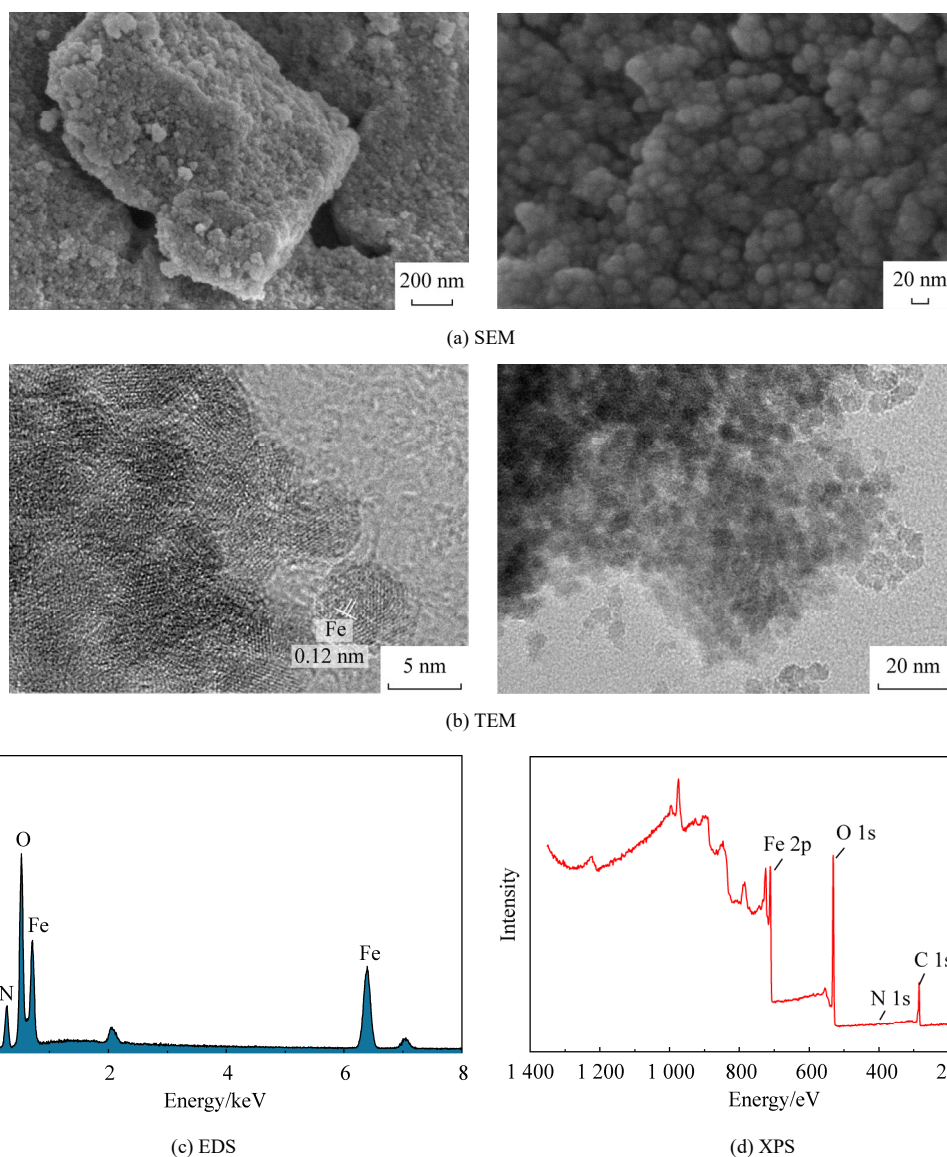


图 2 N/MOF(Fe)的 SEM 照片、TEM 照片、EDS 及 XPS 谱

Fig. 2 Scanning electron microscope (SEM) images, transmission electron microscopy (TEM) images, energy-dispersive spectroscopy (EDS) spectrum and X-ray photoelectron spectroscopy (XPS) spectrum of N/MOF(Fe)

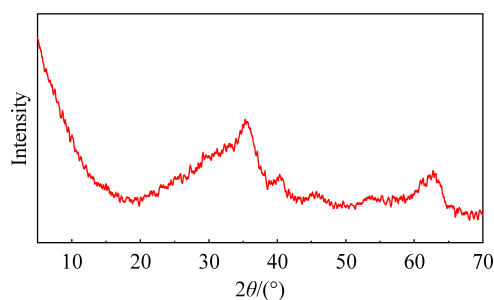
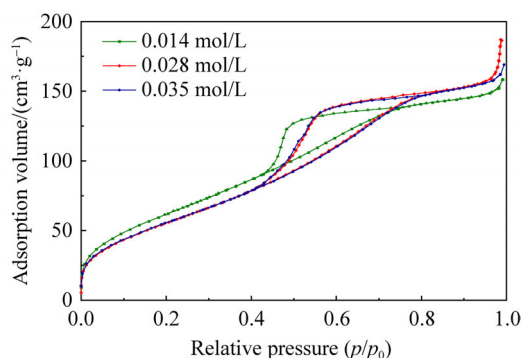
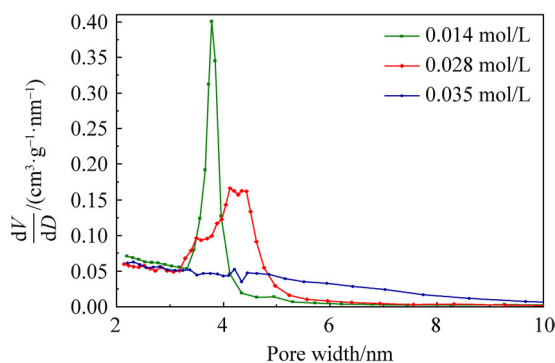


图 3 N/MOF(Fe)的 XRD 谱

Fig. 3 X-ray diffraction (XRD) spectrum of N/MOF(Fe)

(a) N_2 adsorption-desorption isotherms of materials with different urea doping amounts

(b) Pore size distributions of materials with different urea doping amounts

图 4 不同尿素掺杂量的材料的 N_2 吸附脱附等温线和孔径分布图Fig. 4 N_2 adsorption-desorption isotherms and pore size distributions of materials with different urea doping amounts

表 2 不同尿素掺杂量的材料的 BET 分析

Table 2 BET analysis of materials with different urea doping amounts

Urea doping amount/(mol·L ⁻¹)	BET specific surface area/(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Average aperture/nm	Efficiency of adsorption/%
0.014	236.89	0.263	2.07	89.01
0.028	216.59	0.338	2.77	96.82
0.035	216.53	0.272	2.45	96.50

2.3 N/MOF(Fe)吸附 Cr^{6+} 性能

2.3.1 N/MOF(Fe)吸附 Cr^{6+} 实验条件优化 考察了 Cr^{6+} 初始浓度、N/MOF(Fe) 投加量、溶液初始 pH 值和共存离子对 N/MOF(Fe) 吸附性能的影响。如图 5a 所示, 随着 Cr^{6+} 初始浓度的升高, N/MOF(Fe) 吸附效果逐渐下降。当 Cr^{6+} 初始浓度为 5 mg/L 时, N/MOF(Fe) 的吸附能力最佳, 说明此时 N/MOF(Fe) 的吸附点位已得到最大化利用。 Cr^{6+} 去除率随着投加量的增加而升高, 如图 5b 所示。增大投加量可以提高活性吸附点位的数量, 但当投加量由 0.8 g/L 提高到 1.0 g/L 时, 吸附率仅仅提升了 2%。图 5c 为溶液 pH 值对 N/MOF(Fe) 材料吸附性能的影响, 结果表明 N/MOF(Fe) 在酸性条件下的吸附效果要明显优于中性和碱性条件。碱性条件不利于 N/MOF(Fe) 吸附 Cr^{6+} , 这是由于 Cr^{6+} 在水溶液中以带负电 HCrO_4^-

径分布图也证明了这一点。在中压力区 N/MOF(Fe) 的 N_2 吸附量出现拐点, 表明有毛细凝聚现象发生^[18]。尿素掺杂量为 0.028 mol/L 的 N/MOF(Fe) 孔容、孔径最大, 主要分布在 5 nm 左右, TEM 照片也证实了该结论。表 2 为不同尿素掺杂量的材料的 BET 分析。由表 2 可知, 随着尿素掺杂量的增大, N/MOF(Fe) 的孔体积和孔径先增大后减小, 吸附效果也是先增大后减小, 证明了 N/MOF(Fe) 材料的孔径和孔容与吸附性能呈现正相关性^[19]。

的形式存在^[20], 而 N/MOF(Fe) 在酸性条件下带正电, 静电作用促使 N/MOF(Fe) 吸附 Cr^{6+} , 随着 pH 值的升高, 静电作用逐渐减弱, 吸附能力下降^[21]。如图 5d~图 5e 所示, 随着共存离子浓度增加, 吸附率降低幅度不大, Cl^- 、 NO_3^- 、 Na^+ 、 Ca^{2+} 、 Mg^{2+} 对 Cr^{6+} 的吸附只有轻微的抑制作用, 而 SO_4^{2-} 对 Cr^{6+} 的吸附影响显著。这是因为 SO_4^{2-} 为 -2 价, 相比溶液中的铬氧酸根静电引力更强^[22], Cl^- 和 NO_3^- 与铬氧酸根同为 -1 价, 因此 SO_4^{2-} 的竞争吸附效应更明显。吸附率下降了 70%, 表明静电作用在 N/MOF(Fe) 吸附 Cr^{6+} 过程中有重要作用, 其他共存离子存在时吸附率略有降低。

2.3.2 再生实验 为了研究 N/MOF(Fe) 的可回收性, 采用 0.05 mol/L 的 HCl、 CH_3COOH 、 $\text{NH}_3\cdot\text{H}_2\text{O}$ 和 NaOH 溶液对吸附饱和 1 次的 N/MOF(Fe) 进行

再生(见图 6a~见图 6b), HCl 效果最佳, 表明 pH 值对 N/MOF(Fe)的再生起重要作用。N/MOF(Fe)再生 5 次后吸附率仍达到 70%, 这说明 N/MOF(Fe)具备良好重复利用价值, 吸附率的降低的原因为活性位点被占据, 无法完全洗脱 Cr^{6+} 。图 6c 为 N/MOF(Fe)再生前后的 N_2 吸附-脱附曲线, 研究

发现, 再生 2 次后的材料与再生前的材料具有相似的 N_2 吸附脱附曲线, 再生前后 N/MOF(Fe)材料的 BET 信息如表 3 所示。可以看出, 再生后材料的孔径、孔容和比表面积均略有减小, 吸附性能略有下降, 表明再生过程对材料微观结构有轻微影响。

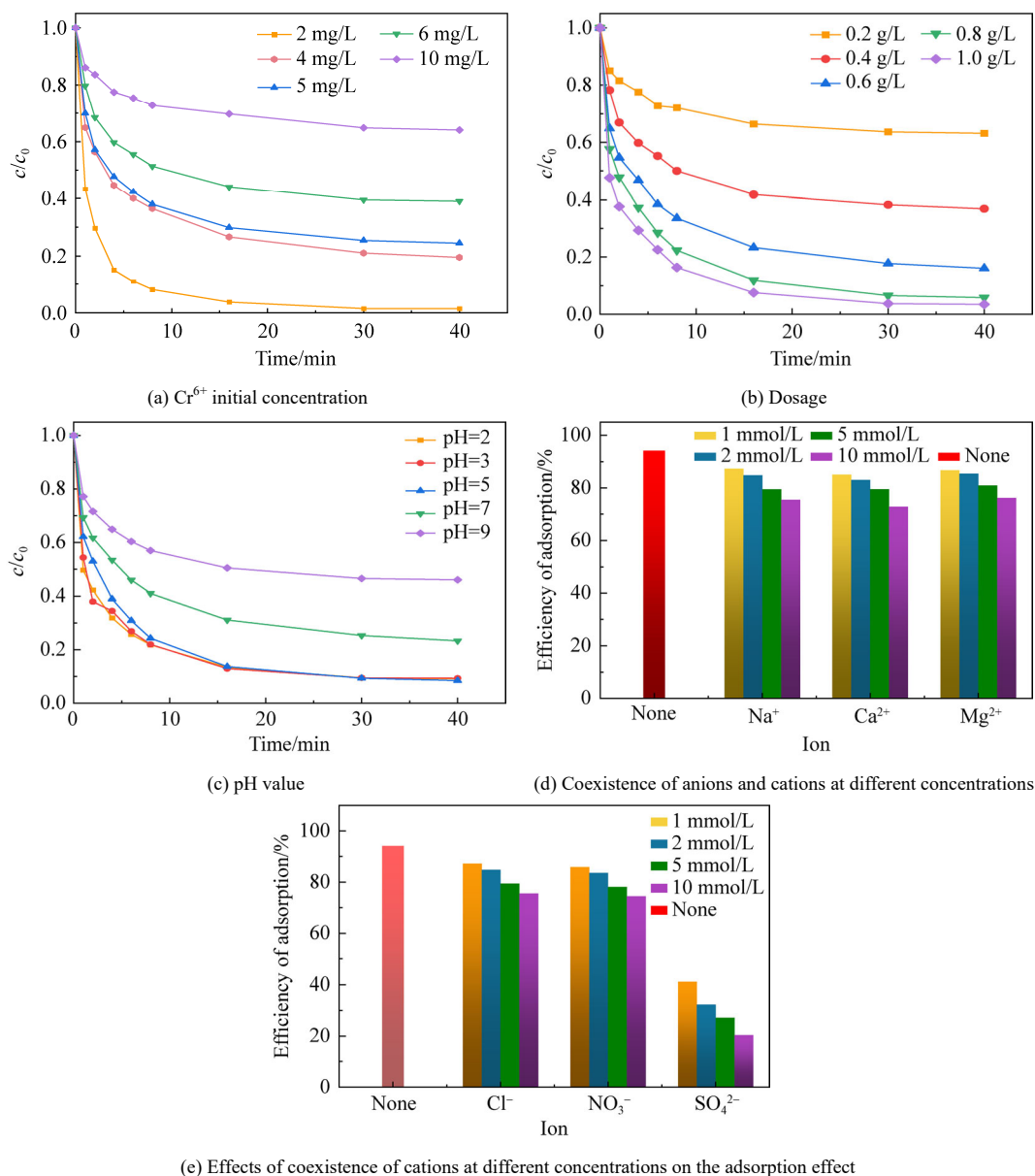


图 5 Cr^{6+} 初始浓度、投加量、初始 pH 值、不同浓度共存阴、阳离子对 N/MOF(Fe) 吸附效果的影响

Fig. 5 Effects of Cr^{6+} initial concentration, dosage, initial pH value, and coexistence of anions and cations at different concentrations on the adsorption effect and efficiency of N/MOF(Fe)

2.4 N/MOF(Fe) 吸附动力学方程、热力学方程和吸附等温线

2.4.1 吸附动力学方程 根据式(3)、(4)、(5)对一、二级动力学方程和颗粒内扩散模型进行拟合^[23], 结果见图 7a~图 7c。二级动力学方程拟合度更高, 表

明吸附过程更符合二级动力学方程。颗粒内扩散模型把吸附过程分为表面扩散、内扩散、吸附平衡 3 个阶段^[24], 吸附过程中 3 个阶段的斜率逐渐减小, 表明反应速率也随之降低, 直至吸附平衡, 截距均不为 0, 反映了表面扩散并不是唯一的限速步骤^[25]。

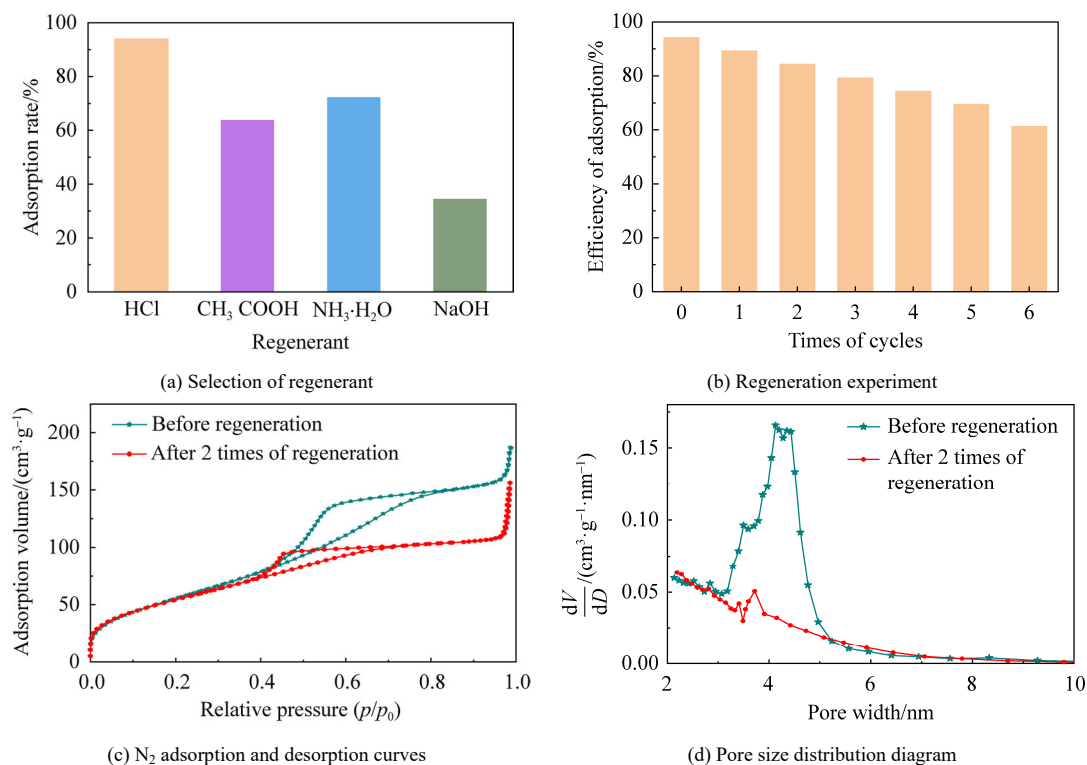
图 6 再生剂的选择, 再生实验, N/MOF(Fe)再生前与再生 2 次后的 N₂ 吸附脱附曲线和孔径分布图Fig. 6 Selection of regenerant, regeneration experiment, N₂ adsorption and desorption curve and pore size distribution diagram of N/MOF(Fe) before regeneration and after regeneration twice

表 3 N/MOF(Fe)再生前与再生 2 次的 BET 分析

Table 3 BET analysis of N/MOF(Fe) before regeneration and after regeneration twice

Sample	BET specific surface area/(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Average aperture/nm	Efficiency of adsorption/%
Before regeneration	216.59	0.338	2.77	95.23
After 2 times of regeneration	204.53	0.222	2.39	84.31

$$\ln \frac{c_0}{c_t} = K_a t \quad (3)$$

$$\frac{1}{c_t} - \frac{1}{c_0} = K_b t \quad (4)$$

$$Q_t = K_c t^{\frac{1}{2}} + C \quad (5)$$

式中: t 为吸附时间, min; K_a 、 K_b 、 K_c 为一、二级动力学和颗粒内扩散模型反应速率常数, min⁻¹; Q_t 为 t 时刻的吸附容量, mg 每 1 g N/MOF(Fe); C 为常数; c_0 、 c_t 分别为初始和 t 时刻时 Cr⁶⁺ 浓度 (mg/L)。

2.4.2 吸附热力学方程 利用式(6)、(7)、(8)进行了热力学数值计算, 见表 4。

$$K_h = \frac{Q_e}{C_e} \quad (6)$$

$$\ln K_h = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

式中: K_h 为固液分配系数; Q_e 为吸附平衡时的吸附容量, mg/g; C_e 为吸附平衡时 Cr⁶⁺ 的去除率; T 为绝对温度, K; R 为理想气体常数, J/(K·mol); ΔG 、 ΔH 、 ΔS 分别为 Gibbs 自由能变、焓变和熵变。结果表明温度的升高不利于吸附进行, 3 个温度下的 ΔG 均为负值, 表明 N/MOF(Fe)可以自发地吸附 Cr⁶⁺。计算得出的 ΔG 值在 -20~0 kJ/mol 范围内, 表明吸附过程中存在物理吸附^[26], ΔH 与 ΔS 小于 0, 说明吸附过程是放热的, 且混乱程度不断减弱。

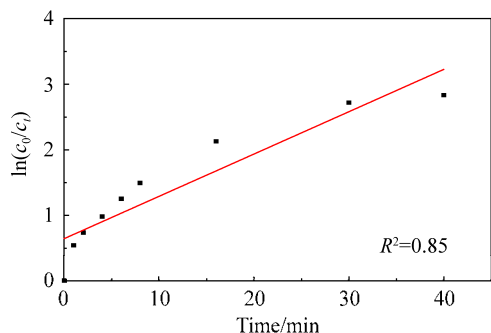
2.4.3 吸附等温线模型 根据以下公式拟合了 3 种吸附等温线模型, 具体参数如表 5 所示。相比于 Freundlich 和 Temkin 模型, Langmuir 模型的相关系数最高, 表明 Cr⁶⁺ 吸附主要为单分子层吸附^[27]。

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (9)$$

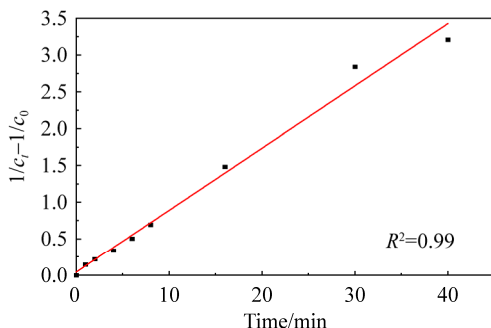
$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (10)$$

$$Q_e = a \ln K_T + a \ln C_e \quad (11)$$

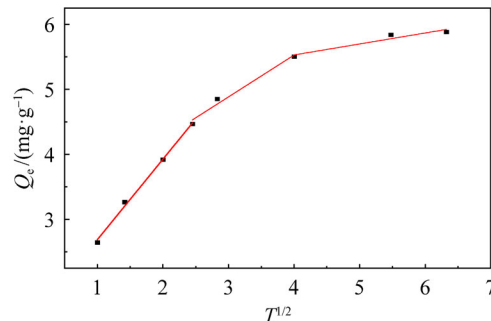
式中: Q_m 为吸附最大时的吸附容量, mg/g; K_L 、 K_F 、 K_T 是 Langmuir、Freundlich 和 Temkin 经验常数; n 、 a 为吸附热相关常数。



(a) First-order kinetic model



(b) Second-order kinetic model



(c) Intraparticle diffusion model

图 7 动力学模型拟合: 一级动力学模型、二级动力学模型、颗粒内扩散模型

Fig. 7 Kinetic model fitting: First-order kinetic model, second-order kinetic model, intraparticle diffusion model

2.4.4 机理分析 为了研究吸附过程中 Cr^{6+} 的价

态变化,对吸附前后 N/MOF(Fe)进行了 XPS 表征。由图 8a 可见,吸附前的 N/MOF(Fe)XPS 全谱显示材料中含有 C、N、O、Fe 元素,证明材料制备成功。吸附后的 XPS 全谱出现了 Cr^{6+} 的特征峰,证实 Cr^{6+} 被吸附在材料表面。由图 8b 可见,吸附前 C 1s 谱在 284.80、286.10、288.52 eV 处有 3 个特征峰,分别对应 C—C、C—N、C—O; 吸附后 3 个特征峰的结合能略有降低,说明复合材料中的官能团参与了 Cr^{6+} 吸附过程^[28]。图 8c 为 N 1s 窄谱,对其进行拟合分峰,出现的 2 个峰分别代表 C=N 和—NH 的特征峰。吸附后—NH 峰消失,证实—NH 参与了 Cr^{6+} 的吸附反应。图 8d 为材料吸附前后 O 1s 分峰拟合情况,吸附后的 3 个特征峰均向更高的能级转移,Fe—O 由 529.89 eV 移动到 530.35 eV, C—O 由 530.43 eV 移动到 530.85 eV, C=O 由 531.59 eV 移动到 531.82 eV,这可能是形成了更稳定的结合物导致的^[29]。图 8e 为材料吸附前后 Fe 的分峰拟合情况,吸附前 Fe 2p 分峰为 Fe 2p_{3/2} (710.67 eV)和 Fe 2p_{1/2} (724.13 eV), Fe 2p_{3/2} 与 Fe 2p_{1/2} 的结合能差距在 14 eV 左右,表明 N/MOF(Fe)的铁元素为 3 价态^[30],吸附后的 Fe 2p 谱表明吸附过程中铁元素的价态没有变化。图 8f 为吸附后 Cr^{6+} 的分峰拟合, Cr^{6+} 可拟合为 2 个特征峰, 577.19 eV 处的 Cr 2p_{3/2} 是 Cr^{3+} , 581.65 eV 处的 Cr 2p_{3/2} 是 Cr^{6+} , Cr 元素原子含量为 0.13%。经过质量守恒计算发现 XPS 结果与反应前后 Cr 元素相对应,表明 Cr 是被吸附在材料的表面,进一步证明了反应过程符合 Langmuir 吸附等温模型。

表 4 N/MOF(Fe)吸附 Cr^{6+} 的热力学参数

Table 4 Thermodynamic parameters of Cr^{6+} adsorption by N/MOF(Fe)

T/K	$K_h/(\text{m}^3 \cdot \text{g}^{-1})$	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
298	20.586	-7.742	-27.211	-65.331
313	16.616	-6.762	-27.211	-65.331
328	7.463	-5.782	-27.211	-65.331

T is absolute temperature. K_h is solid-liquid distribution coefficient. ΔG is Gibbs free energy change. ΔH is enthalpy change. ΔS is entropy change.

表 5 N/MOF(Fe)吸附 Cr^{6+} 的等温线参数

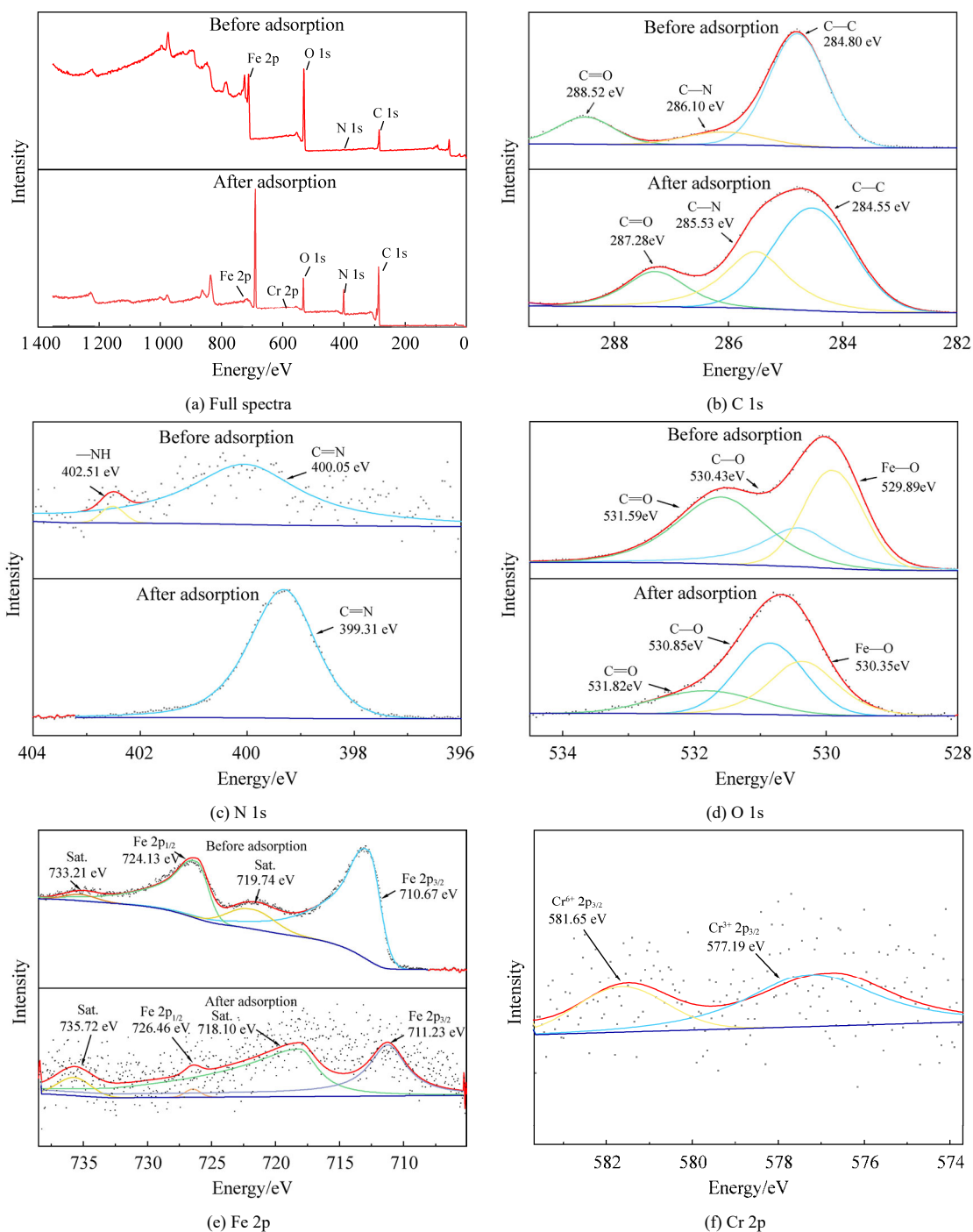
Table 5 Isotherm parameters of N/MOF(Fe) adsorbing Cr^{6+}

Langmuir			Freundlich			Temkin		
$K_L/(\text{L} \cdot \text{mg}^{-1})$	$Q_m/(\text{mg} \cdot \text{g}^{-1})$	R^2	$K_F/(\text{mg} \cdot \text{g}^{-1})$	n	R^2	$K_T/(\text{L} \cdot \text{g}^{-1})$	$a/(\text{J} \cdot \text{mol}^{-1})$	R^2
85.631	7.299	0.999	6.411	8.13	0.847	18.051	0.671	0.837

K_L is empirical constant of Langmuir. K_F is empirical constant of Freundlich. K_T is empirical constant of Temkin. Q_m is adsorption capacity at maximum adsorption. n and a is adsorption heat related constant. R^2 is variance.

图 9a 为 Cr^{6+} 在反应过程中的质量守恒情况。由图 9a 可见, 溶液中存在一定的 Cr^{3+} , 说明吸附过程伴随着 Cr 的还原, 验证了 XPS 谱的分析结果。图 9b 研究了吸附过程中还原 Cr^{6+} 的主要物种。选择对苯醌(BQ)为超氧自由基($\cdot\text{O}_2^-$)捕获剂, 只加入 BQ 时, 大约 16% 的 Cr^{6+} 被还原, 但同时加入 N/MOF(Fe) 和 BQ 时, Cr^{6+} 去除率比单独加入 N/MOF(Fe) 时提

升了 11%, 这说明反应体系存在还原性物质 $\cdot\text{O}_2^-$ 。 $\cdot\text{O}_2^-$ 的产生可能来自于转子与玻璃和 N/MOF(Fe) 之间的摩擦^[31], 摩擦过程中产生了 $\cdot\text{O}_2^-$, 参与了 Cr^{6+} 的还原。由于产生的 $\cdot\text{O}_2^-$ 较少, 剩余 69.08% 的 BQ 会与 Cr^{6+} 反应导致去除率升高, 可能的反应式如式(12)、(13)所示。综上所述, 提出了 N/MOF(Fe) 结构模型和吸附 Cr^{6+} 的机理图(见图 9d)。



Sat is satellite peaks.

图 8 N/MOF(Fe)吸附前后的 XPS 谱
Fig. 8 XPS spectra before and after N/MOF(Fe) adsorption

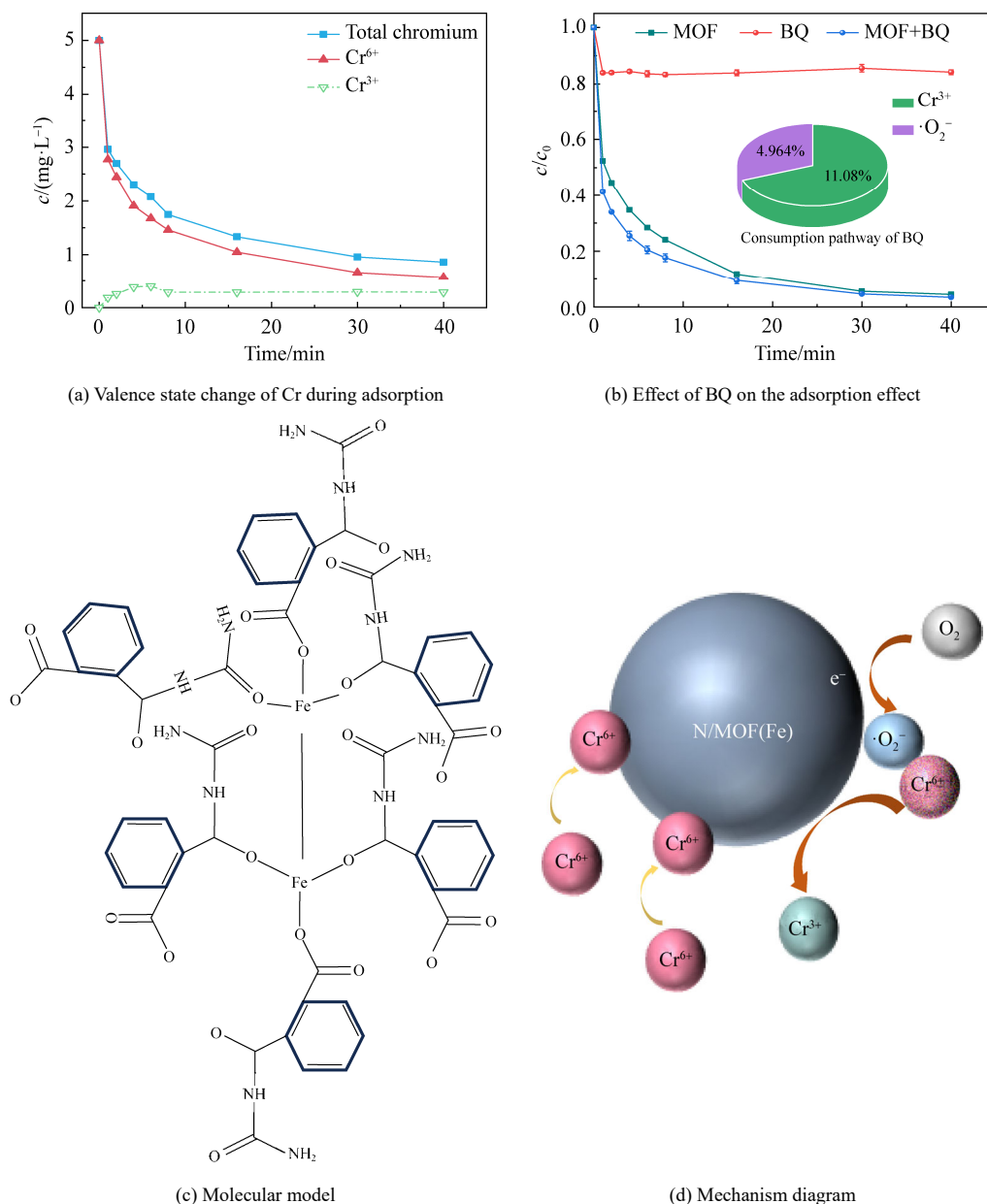


图9 N/MOF(Fe)吸附时Cr的价态变化、BQ对吸附效果影响、分子模型及机理图

Fig. 9 Valence state change of Cr during adsorption, effect of benzoquinone (BQ) on the adsorption effect, molecular model and mechanism diagram

3 结论

使用尿素为结构剂对MOF(Fe)进行改性, 通过溶剂热法制备了N/MOF(Fe)。在最佳条件水力条件下, N/MOF(Fe)对 Cr^{6+} 的吸附率可达95.23%, 吸附容量可达8.1 mg/g。吸附反应符合二级反应动力学方程, 吸附模型符合Langmuir模型, 吸附反应为自发的放热反应。N/MOF(Fe)具有良好的再生性能, 吸附过程伴随着物理化学反应, 该过程实现了N/MOF(Fe)对 Cr^{6+} 的原位吸附和还原, 与传统的吸附剂相比更加绿色环保。

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In situ Adsorption–Reduction of Cr⁶⁺ with N/MOF(Fe) Adsorbent

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Extended Abstract

Introduction Accompanied by industrial production, the issue of hexavalent Cr⁶⁺ contamination in water environments is becoming increasingly severe. The adsorption method for removing Cr⁶⁺ from water has attracted attention due to its operational simplicity and low cost. MOF as adsorbents possess structural advantages such as large surface area and high porosity. Hybridization of MOF can increase the adsorption sites, enhance reaction activity, and further improve the adsorption performance of MOF. Research on synthesizing MOFs using KHP as an organic ligand is scarce. In this study, KHP was utilized as the organic ligand to synthesize urea-doped N/MOF(Fe) via a solvothermal method. The optimal urea doping concentration of N/MOF(Fe) was characterized using SEM, TEM, BET, XRD, XPS, and other techniques. The effects of factors such as the initial concentration of Cr⁶⁺, the dosage of N/MOF(Fe), the initial pH of the solution, the presence of coexisting ions on the adsorption reaction, and the corresponding mechanisms, were analyzed. The adsorption kinetic equation was established, the adsorption isotherm model, and adsorption thermodynamic parameters, were calculated.

Methods After determining the optimal preparation conditions for MOF(Fe) through orthogonal experiments, a solution was prepared by adding 0.306 g of KHP 1.212 g of Fe(NO₃)₃·9H₂O, 0.6 mL of acetic acid, and 0.028 mmol/L of urea into 24 mL of DMF. The solution was stirred until completely dissolved and then transferred to a reaction vessel lined with PTFE. The reaction was carried out at 180 °C for 20 h. Afterward, a reddish-brown precipitate was obtained by centrifugation. The precipitate was washed several times with deionized water and ethanol, followed by drying overnight at 80 °C. The resulting material was named as N/MOF(Fe). A certain amount of the adsorbent was added to a 140 mL solution of Cr⁶⁺. At specific intervals, aliquots of the solution were taken out and the absorbance was measured to study the N/MOF(Fe) adsorption behavior.

Results and discussion Orthogonal experiments indicate that controlling the pH value is crucial for the adsorption of Cr⁶⁺ by MOF(Fe). The optimal preparation conditions for MOF(Fe) are a reaction temperature of 180 °C, a reaction time of 20 hours, a metal-to-ligand molar ratio of 1.0:0.7, and a pH value of 2.3. After urea doping, the material's adsorption capacity and adsorption rate were significantly enhanced. When the urea doping concentration was 0.028 mol/L, the adsorption rate of N/MOF(Fe) reached its maximum. N/MOF(Fe) exhibited a spherical structure with a lattice spacing of 0.12 nm. The diffraction peaks were broad, indicating low crystallinity and diffraction intensity. BET analysis showed that the adsorption of N/MOF(Fe) followed a type II isotherm with a hysteresis loop, indicating primarily mesoporous characteristics with pore size distribution mainly around 5 nm. With the increase in urea doping concentration, the pore volume and pore size of N/MOF(Fe) first increased and then decreased. The adsorption effect followed the same trend. Characterization by XRD and XPS revealed that the Fe³⁺ present in N/MOF(Fe) did not undergo a change in oxidation state during the adsorption process. There was a certain amount of Cr³⁺ in the solution.

The optimal experimental conditions were found to be an initial Cr⁶⁺ concentration of 5 mg/L, an adsorbent dosage of 0.8 g/L, and no adjustment of the initial pH of the solution. Electrostatic interactions enabled N/MOF(Fe) to exhibit superior adsorption performance in acidic environments. The SO₄²⁻ being divalent, exerted stronger electrostatic attraction compared to chromate ions in the solution, leading to a more significant competitive adsorption effect. Apart from SO₄²⁻, other coexisting ions have little effect on the adsorption of N/MOF(Fe). BET analysis indicated that the material regenerated twice exhibited similar N₂ adsorption-desorption isotherms to the original material. The regeneration process had a slight effect on the pore size, pore volume, and specific surface area of N/MOF(Fe), but it did not significantly affect its adsorption performance. N/MOF(Fe) demonstrated good repeatability in reuse tests, with the adsorption rate remaining at around 70% even after multiple regenerations. The *n* in the Freundlich model is 8.13, indicating that the adsorption process is the main chemical adsorption and is easy to occur. In the intra-particle diffusion model, the intercepts of all three stages were non-zero, reflecting that surface diffusion is not the only limiting step. The *a* in the fitting result of Temkin model is 0.671, which proves that the adsorption of Cr⁶⁺ by N/MOF(Fe) is an exothermic process. By BQ, the mechanism of Cr⁶⁺ adsorption by N/MOF(Fe) was investigated, revealing the involvement of ·O₂⁻ in the reduction of Cr⁶⁺ during the adsorption process.

Conclusions Urea was employed as a structure-directing agent to modify MOF(Fe), resulting in the preparation of N/MOF(Fe) via a solvothermal method. The adsorption reaction followed a second-order kinetic equation, and the adsorption model conformed to the Langmuir model. The adsorption process was characterized as a spontaneous exothermic reaction. N/MOF(Fe) demonstrated excellent regeneration performance, with the adsorption process involving physicochemical reactions. This process facilitated the in-situ adsorption and reduction of Cr⁶⁺ by N/MOF(Fe), rendering it more environmentally friendly compared to traditional adsorbents.

Keywords metal organic framework; hexavalent chromium; adsorption; urea