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# 聚多巴胺修饰矸石基沸石净化含镉污水性能与机制

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**摘要**：针对传统沸石合成成本高且表面缺乏特异性吸附位点的问题,以煤矸石为研究对象,多巴胺为聚合单体,采用水热法-表面自聚合反应制备了聚多巴胺改性矸石基沸石(Zeolite@PDA)用于水中镉的高效吸附去除,通过静态吸附实验研究了改性前后沸石的吸附性能,运用 SEM-EDS 和 XPS 表征手段揭示了其对水中 Cd(Ⅱ)的吸附机制.结果表明,聚多巴胺涂层显著提高了煤矸石基沸石对 Cd(Ⅱ)的吸附能力.Zeolite@PDA 吸附 Cd(Ⅱ)的过程更符合 Langmuir 吸附等温模型和准二级动力学模型,说明吸附过程是单层的化学吸附,且理论上最大吸附量可达 130.89mg/g,约为矸石基沸石的 2 倍($q_{max}$=66.49mg/g).热力学研究表明 Zeolite@PDA 吸附 Cd(Ⅱ)是自发,吸热且固液界面紊乱度增加的过程.SEM-EDS 和 XPS 表征显示,Zeolite@PDA 对 Cd(Ⅱ)的去除机理包括沸石中 $Na^+$ 与 Cd(Ⅱ)的离子交换反应和聚多巴胺涂层官能团与 Cd(Ⅱ)的表面络合作用.

**关键词**：煤矸石；沸石；镉；吸附性能；吸附机制
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**Adsorption performance and mechanisms of Cd(Ⅱ) from aqueous solution by polydopamine modificated coal gangue-derived zeolite.** ZHOU Yu-zhi[1,2], LONG Lin-li[1], HU Pian[1], SUN Jing-yu[1], NIU Jing-wei[1], CHEN Min[3], WANG Wen-shuo[1], CHEN Xiao-yang[1,2*] (1.State Key Laboratory for Safe Mining of Deep Coal Resources and Environment Protection, Anhui University of Science and Technology, Huainan 232001, China；2.School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China；3.Taizhou Institute of Zhejiang University, Zhejiang University, Taizhou 318000, China). *China Environmental Science*, 2025,45(7)：3762~3770

**Abstract**：To solve the problems of high synthesis cost and lack of specific adsorption sites on traditional zeolites surface, polydopamine-modified coal gangue based zeolite was successfully synthesized by combining alkali melting hydrothermal method and impregnation coating method using coal gangue as raw material and dopamine as the polymerization monomer and applied for efficient adsorption of Cd(Ⅱ) from aqueous solution. The adsorption performance was investigated by batch adsorption experiments, and adsorption mechanism was revealed by SEM-EDS and XPS method. The results showed that polydopamine coating significantly improved the adsorption capacity of coal gangue-derived zeolite. The adsorption process conformed to the Langmuir adsorption isotherm model and pseudo-second-order model, suggesting that Cd(II) adsorption by Zeolite@PDA was monolayer and chemical adsorption, and the theoretical maximum adsorption capacity could reach 130.89mg/g, which was two times as high as that of Zeolite ($q_{max}$=66.49mg/g). Thermodynamic studies indicated that Cd(II) adsorption by Zeolite@PDA was a spontaneous, endothermic process with increased disorder at the solid-liquid interface. SEM-EDS and XPS analysis showed that cation exchange between $Na^+$ and Cd(II) as well as surface complexation between surface functional groups and Cd(II) played a primary role for Cd(II) removal.
**Key words**：coal gangue；zeolite；Cd；adsorption performance；adsorption mechanisms

镉(Cd)被发现是毒性最强的重金属之一,其主要来源于金属矿开采,金属电镀,冶炼加工等行业[1].目前,对于含重金属废水的处理技术主要有化学沉淀法,蒸发浓缩法,膜分离法,生物法,吸附法等[2-5].吸附法由于具有原料来源广泛,过程绿色环保,操作简单,设备要求低等优点而受到广泛关注.现阶段已开发出许多吸附剂用于重金属镉的去除,比如碳纳米管[6],环氧树脂[7],氧化石墨烯[8]等,但这些吸附材料往往因存在吸附位点少,成本高,比表面积小等缺点导致其在环境污染修复领域的应用受到限制.

煤矸石是煤炭开采过程中产生的大宗固体废

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物,考虑到煤矸石主要成分是 $SiO_2$ 和 $Al_2O_3$,大量学者以煤矸石为原料,采用不同的合成方法制备了不同类型的沸石分子筛,并将其用于水体中各种污染物的去除[9].但是纯沸石存在表面吸附位点少,吸附性能较差问题,亟需对其进行改性以增加表面官能团密度,提高其对水体中潜在有毒元素的吸附性能[10].

受海洋贻贝表面化学的启发,聚多巴胺涂层作为一种有效的改性手段,具有反应条件温和,活性基团丰富,生物相容性好等优点[11-12],已广泛应用于生物矿化[13],锂离子电池[14],纳米材料功能化[15],环境修复[16]等领域.比如 Wu 等[17]以磁性纳米颗粒和介孔碳为基底制备了聚多巴胺功能化吸附剂;Fu 等[18]制备了聚多巴胺微球,在 25℃时吸附量可达 90.7mg/g;朱建康等[19]运用 PDA 对氟化石墨烯进行修饰,以提升涂层防腐性能;李琦等[20]将聚多巴胺和 ZnO 结合形成 PDA/ZnO 复合阴极缓冲层,以此提高太阳能电池器件的性能.目前,以煤矸石为原料制备聚多巴胺改性沸石的研究鲜有报道,聚多巴胺涂层对煤矸石基沸石理化性质和吸附特性的影响尚不明确,对 Cd(Ⅱ)的吸附机理有待进一步探究.

因此,本研究将仿生聚多巴胺用于修饰煤矸石基沸石,增加沸石表面邻苯二酚,邻苯二醌,胺基,亚胺基等活性基团,从而赋予沸石材料新的表面性质,并提高其对 Cd(Ⅱ)的吸附性能,以期实现大宗固废的资源化利用和重金属废水净化.

## 1　材料与方法

### 1.1　材料

氢氧化钠,盐酸,硝酸镉,无水乙醇均为分析纯,购自国药化学试剂有限公司(上海);盐酸多巴胺和三(羟甲基)氨基甲烷为优级纯,购自阿拉丁试剂(上海)有限公司.煤矸石取自安徽省淮南市平圩电厂,其物质组成见表 1.煤矸石中 $Al_2O_3$ 和 $SiO_2$ 的占比高于 90%,且 $Al_2O_3$ 和 $SiO_2$ 的比值为 2.22.

**表 1　煤矸石的组成成分**

Table 1　Composition of coal gangue

| 化学组成 | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $K_2O$ | $TiO_2$ | MgO | $Na_2O$ | CaO | 其它 |
|---|---|---|---|---|---|---|---|---|---|
| 含量(%) | 64.12 | 28.85 | 2.77 | 1.44 | 0.835 | 0.748 | 0.747 | 0.21 | 0.28 |

### 1.2　聚多巴胺修饰矸石基沸石的制备

**1.2.1　矸石基沸石的制备**　将采集的煤矸石样品球磨处理 2h,过 100 目筛,获得煤矸石粉末;将上述煤矸石粉末与氢氧化钠按照 1:1.2 质量比混合,研磨后,置于马弗炉中,在 500℃下焙烧 3h,得到灰白色固体;将获得的灰白色固体按照固液比为 1:20 加入到 3mol/L 的 NaOH 溶液中,磁力搅拌 12h,接着将混合溶液转移至高压反应釜中,在 105℃下水热反应 12h 后,将沉淀过滤和洗涤后,在 60℃下烘干,即得矸石基沸石材料,记为 Zeolite.

**1.2.2　聚多巴胺修饰沸石的制备**　将 0.6g 矸石基沸石加入到 100mL 乙醇水溶液(体积比为 1:1)中,混合均匀后,加入 0.4g 盐酸多巴胺进行搅拌.然后,将 10mL 20mmol/L Tris(三羟甲基氨基甲烷)缓冲液逐滴加入,调节 pH 值至 8.5 后分别搅拌 10,30,60,120min,离心,洗涤沉淀,即得具有不同涂层厚度的聚多巴胺修饰沸石,分别记为 Zeolite@PDA−1,Zeolite@PDA−2,Zeolite@PDA−3,Zeolite@PDA−4.

### 1.3　材料表征

采用傅立叶变换红外光谱仪(FTIR,Thermo Scientific Nicolet iS20)测试修饰前后沸石的红外光谱;采用 X 射线光电子能谱仪(XPS,ESCALAB 250Xi,美国)分析吸附 Cd 前后材料表面元素组成及特定元素的价态;利用 X 射线衍射光谱仪(XRD,Bruker D8,德国)对材料进行物相分析;采用比表面与孔隙度分析仪(BET,NOVAe1200 型,美国)测定材料比表面积和孔径分布;采用热重分析仪(TGA,日本 Rigaku)评估沸石及其改性材料的热稳定性.利用原子吸收分光光度计测定吸附后上清液 Cd 离子浓度.

### 1.4　吸附实验

采用恒温振荡批量吸附实验测定修饰前后沸石对 Cd 的吸附量.称取一定量 Zeolite 和 Zeolite@PDA 于 100mL 硬质离心管中,加入 50mLCd 溶液中,用稀 HCl 或 NaOH 溶液调节 Cd 溶液 pH 值至设定值,然后在 30℃条件下恒温振荡 4h.吸附结束后,抽滤,测定上清液 Cd 的浓度.所有实验数据均采用 3 个平行样的平均值.吸附量 $q_e$(mg/g)和去除率 $R$(%)分别由公式(1)和公式(2)计算得出:

$$q_e = \frac{V \cdot (C_0 - C_e)}{m} \quad (1)$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

式中:$C_0$ 为 Cd(Ⅱ)溶液的初始浓度,mg/L;$C_e$ 为平衡时 Cd(Ⅱ)溶液浓度,mg/L;$m$ 为吸附剂投加量,g;$V$ 为溶液体积,L.

1.4.1 图层厚度的影响实验 分别称取 10mg Zeolite@PDA-1,Zeolite@PDA-2,Zeolite@PDA-3 和 Zeolite@PDA-4 加入到 50mL Cd(Ⅱ)溶液中(50mg/L),30℃下恒温振荡 4h,测定 Cd(Ⅱ)的浓度.

1.4.2 pH 值影响实验 称取 10mg 吸附剂分散于 50mL 50mg/L 的 Cd(Ⅱ)溶液,然后调节溶液 pH 值为 2,3,4,5,6,7,30℃下恒温振荡 4h,测定 Cd(Ⅱ)的浓度.

1.4.3 吸附剂添加量影响实验 量取 50mL Cd(Ⅱ)溶液(50mg/L,pH=7.0)于 100mL 离心管中,分别加入 5,10,20,30,40,50mg 吸附剂,30℃下恒温振荡 4h,测定 Cd(Ⅱ)的浓度.

1.4.4 吸附等温实验 称取 10mg 吸附剂于 100mL 硬质离心管中,加入 50mL 浓度分别为 20,40,60,80,120,160,200,300mg/L 的 Cd(Ⅱ)溶液(pH=7),30℃下恒温振荡 4h,测定 Cd(Ⅱ)的浓度.

1.4.5 吸附动力学实验 将 10mg 吸附剂分别加入到 50mL Cd(Ⅱ)溶液中(50mg/L,pH=7.0),在 30℃温度条件下分别恒温振荡 15,30,60,120,180,240,480,960,1200,1440min,测定 Cd(Ⅱ)的浓度.

## 2 结果与讨论

### 2.1 材料表征

由图 1(a)可知,煤矸石主要由高岭石,石英和非晶物质组成.经碱熔融-水热处理后,高岭石的衍射峰消失,同时沸石的衍射峰出现(化学式:$Na_2(AlSiO_4)_6 \cdot 4H_2O$,PDF No.42-0216),其所涉及的化学反应如下,这表明煤矸石已成功转化为沸石.根据 Zeolite 和 Zeolite@PDA 的 FT-IR 光谱图(图 1(b)),位于 3483 和 1647cm$^{-1}$ 处有明显的吸收峰,这代表-OH 的伸缩振动[21];位于 1471,1410 和 977cm$^{-1}$ 处的吸收峰,对应于 T-O-T(T=Si/Al)内部不对称和对称伸缩振动[22];569cm$^{-1}$ 处的吸收峰属于双四元环的外部振动[23];719 和 662cm$^{-1}$ 处的吸收峰归因于 Si-OH 和 Al-O 键的对称伸缩振动[24],这也说明沸石成功合成.与 Zeolite 相比,Zeolite@PDA 的 FT-IR 光谱图在 1392cm$^{-1}$ 出现一个属于 PDA 的吲哚啉结构的吸收峰[25],这说明 PDA 已成功修饰于沸石表面.

$$2NaOH + SiO_2 \xrightarrow{\text{fusion}} Na_2SiO_3 + H_2O \quad (3)$$

$$10NaOH + 3Al_2O_3 \cdot 2SiO_2 \xrightarrow{\text{fusion}} 2Na_2SiO_3 + 6NaAlO_2 + 5H_2O \quad (4)$$

$$NaOH(aq) + Na[Al(OH)_4](aq) + Na_2SiO_3(aq) \rightarrow [Na_x(AlO_2)_y \cdot NaOH \cdot H_2O](gel) \rightarrow Na_p[(AlO_2)_p \cdot (SiO_2)_q] \cdot hH_2O(Crystal) \quad (5)$$

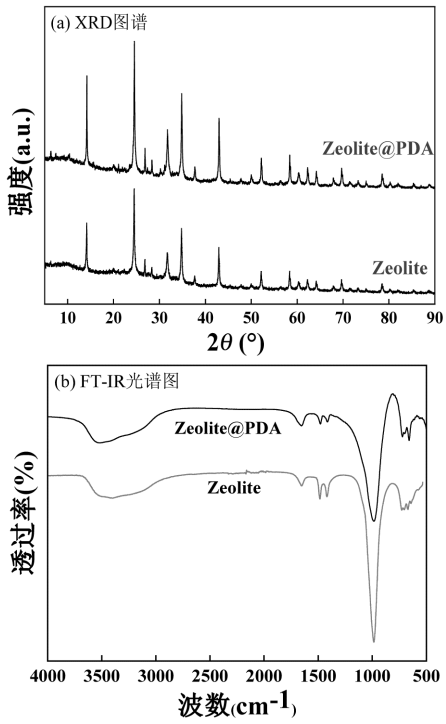



图 1 Zeolite 和 Zeolite@PDA 的 XRD 图谱和 FT-IR 光谱图

Fig.1 XRD patterns and FT-IR profiles of Zeolite and Zeolite@PDA

从图 2(a)可以发现,Zeolite 和 Zeolite@PDA 的 $N_2$ 吸附-脱附等温线接近Ⅳ型,且均在 $P/P_0$=0.4~1.0 范围内存在 $H_3$ 滞后环,说明存在介孔结构.图 2(b)显示,Zeolite 和 Zeolite@PDA 的孔径主要集中于 2~10nm,进一步证实介孔结构的存在.根据 BET 的测量结果,经 PDA 修饰后,Zeolite 的比表面积由 25.1513m$^2$/g 增加到 52.2348m$^2$/g,有利于对污染物的吸附.

由图 3 可以看出,Zeolite 质量损失随温度变化情况可分为 2 个阶段:在室温~220℃温度区间内,Zeolite 的质量损失约为 10%,这归因于物理或化学吸附水的挥发;在 220~800℃范围内,Zeolite 的质

量损失约为 4.46%,这与沸石结晶水的损失有关.整体上看,Zeolite@PDA 的质量损失率为 15.50%,高于 Zeolite 的 14.46%,这与 PDA 涂层的分解有关[26],也进一步说明 PDA 涂层的存在.

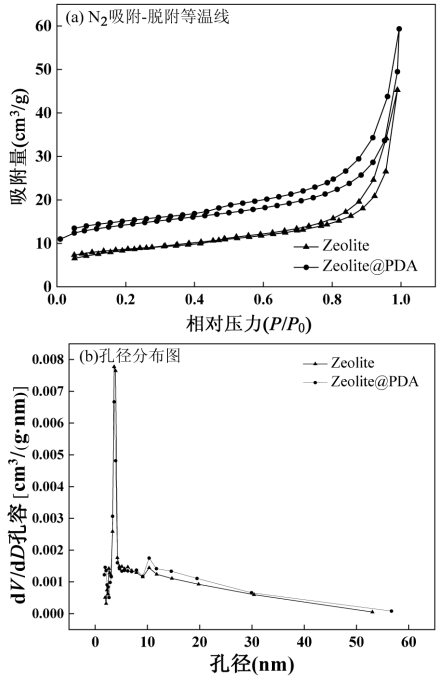



图 2　Zeolite 和 Zeolite@PDA 的 $N_2$ 吸附−脱附等温线和孔径分布

Fig.2　$N_2$ adsorption−desorption isotherms and the distribution of pore size of Zeolite and Zeolite@PDA

**表 2**　Zeolite 和 Zeolite@PDA 的比表面积、孔容和 BJH 孔径

Table 2　BET specific surface, pore volumes and BJH pore size of Zeolite and Zeolite@PDA

| 吸附材料 | 比表面积($m^2$/g) | 孔容($cm^3$/g) | BJH 孔径(nm) |
|---|---|---|---|
| Zeolite | 25.1513 | 0.0616 | 19.1527 |
| Zeolite@PDA | 52.2348 | 0.0784 | 14.7101 |

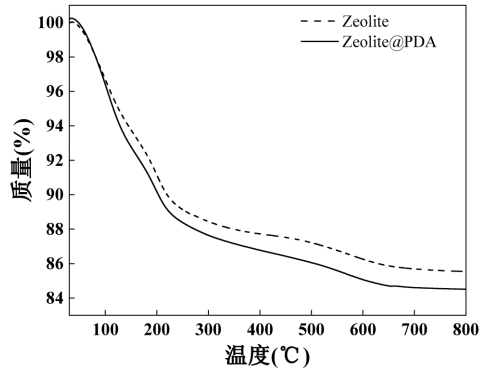



图 3　Zeolite 和 Zeolite@PDA 的热重分析曲线

Fig.3　TG curves of Zeolite and Zeolite@PDA

## 2.2　吸附性能

**2.2.1　图层厚度的影响**　由图 4 可知,Zeolite@PDA 对 Cd(Ⅱ)的吸附量随着涂层厚度的增加呈现先增大后降低的趋势,其原因可能是因为 PDA 富含邻苯二酚,胺基,亚胺基等活性基团,有利于提高沸石的吸附量;而过多的 PDA 涂层会造成沸石孔隙的堵塞,且表面活性吸附位点的数量并未增加,从而降低吸附量.其中,Zeolite@PDA 的吸附量为 84.5~102.7mg/g,高于矸石基沸石的吸附量,这说明聚多巴胺改性有利于提高矸石基沸石的吸附性能.为使后续实验效果达到最佳,选用 Zeolite@PDA−2 作吸附剂(后面统称为 Zeolite@PDA).

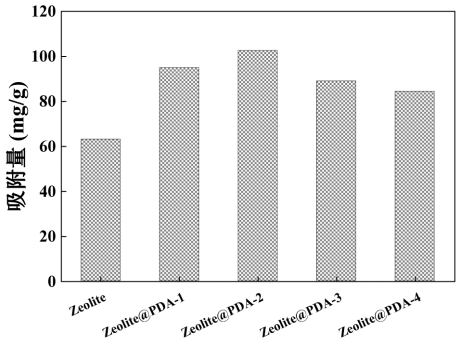
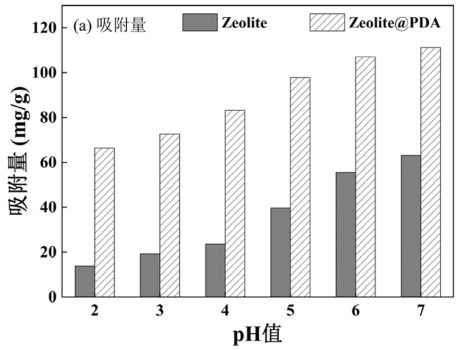



图 4　不同涂层厚度的 Zeolite@PDA 对 Cd(Ⅱ)的吸附量

Fig.4　Adsorption capacity of Cd(II) by Zeolite@PDA at different coating thicknesses

**2.2.2　溶液 pH 的影响**　由图 5 所示,随着溶液 pH 值从 2.0 上升到 7.0,Zeolite 和 Zeolite@PDA 对 Cd(Ⅱ)的吸附量分别由 13.8 和 66.4mg/g 增加到 63.2 和 111.2mg/g;Zeolite 和 Zeolite@PDA 对 Cd(Ⅱ)的去除率分别由 5.52%和 26.56%上升到 25.28%和 44.48%.当 pH 值为 2.0 时,Zeolite@PDA 的吸附量较低,此时溶液中 $H^+$ 与 Cd(Ⅱ)同时竞争吸附剂表面的吸附位点,不利于吸附的进行,而随着溶液 pH 值的上升,溶液中 $H^+$ 对吸附位点的竞争减弱,有利于吸附过程的进行,吸附量增加[27].



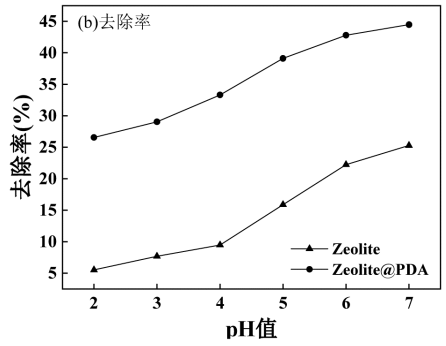
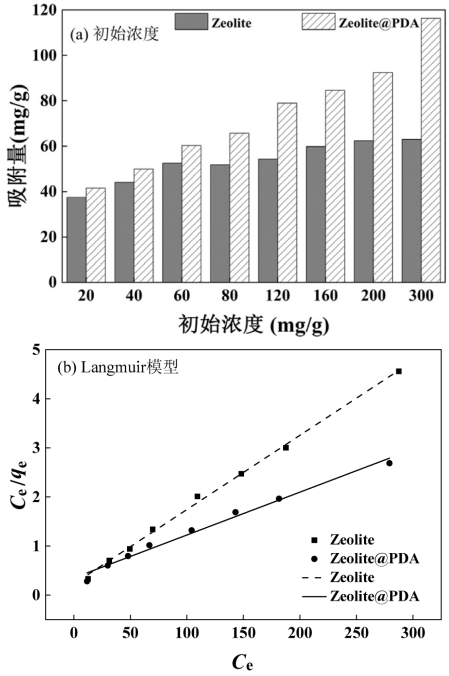



图 5 溶液 pH 值对 Zeolite 和 Zeolite@PDA 吸附 Cd(Ⅱ)的影响

Fig.5 Effect of initial pH values on the Cd(Ⅱ) adsorption by Zeolite and Zeolite@PDA

2.2.3 吸附等温线模型 由图 6(a)可知,随着 Cd(II)初始浓度的增大,对 Cd(Ⅱ)的吸附量逐渐增大,这是由于初始浓度增大,固相与液相离子浓度梯度变大,有利于 Cd(II)由液相向固相吸附剂的迁移;当 Cd(II)初始浓度达到 300mg/g 时,Zeolite 和 Zeolite@PDA 的吸附量分别为 63 和 116.4mg/g.

由图 6(b)和(c)可知,根据拟合 $R^2$,Zeolite 和 Zeolite@PDA 对 Cd(II)的吸附更符合 Langmuir 吸附等温模型,说明该吸附为单分子层吸附[28],且理论饱和吸附容量高达 130.89mg/g,优于其他吸附剂[29-34].根据 Freundlich 等温模型理论,当 0<1/$n$<1 时,吸附容易进行;当 1/$n$>1 时,吸附难以进行.由表 3 可知,1/$n$ 为 0.3,表明 Zeolite@PDA 吸附 Cd(II)易于发生.



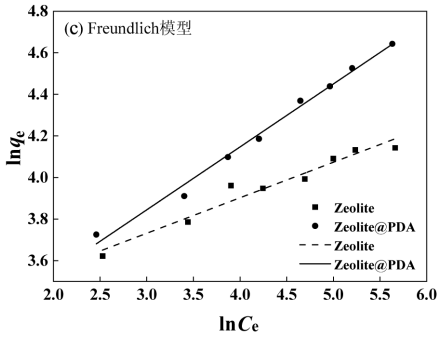




图 6 Zeolite 和 Zeolite@PDA 吸附 Cd(Ⅱ)的等温模型拟合

Fig.6 Isotherms model fitting for Cd(Ⅱ) adsorption by Zeolite and Zeolite@PDA

**表 3 Zeolite 和 Zeolite@PDA 吸附等温线模型拟合参数**

Table 3 Adsorption isotherms fitting parameters of Zeolite and Zeolite@PDA

| 模型 | 参数 | Zeolite | Zeolite@PDA |
|---|---|---|---|
| Langmuir | $q_{max}$(mg/g) | 66.49 | 130.89 |
| | $K_L$(L/mg) | 0.074 | 0.033 |
| | $R^2$ | 0.997 | 0. 994 |
| Freundlich | $K_F$(mg/g) | 24.1632 | 17.9362 |
| | $n$ | 5.65 | 2.89 |
| | $R^2$ | 0.951 | 0.983 |

2.2.4 吸附动力学模型 由图 7 和表 4 可以看出,Zeolite 和 Zeolite@PDA 的准二级动力学模型拟合效果均优于准一级模型,且拟合系数 $R^2$ 均为 0.999.此外,Zeolite 和 Zeolite@PDA 准二级动力学模型导出的平衡吸附量分别为 68.12 和 122.25mg/g,与实验值更为接近,这也进一步表明准二级动力学模型更适合描述吸附过程,说明吸附控制步骤是化学吸附[35].

**表 4 Zeolite 和 Zeolite@PDA 吸附动力学模型拟合参数**

Table 4 Adsorption isotherms fitting parameters of Zeolite and Zeolite@PDA

| 模型 | 参数 | Zeolite | Zeolite@PDA |
|---|---|---|---|
| 准一级动力学模型 | $q_e$ (mg/g) | 57.53 | 108.91 |
| | $k_1$(min$^{-1}$) | 0.0156 | 0.0227 |
| | $R^2$ | 0.948 | 0.801 |
| 准二级动力学模型 | $q_e$ (mg/g) | 68.12 | 122.25 |
| | $k_2$[g/(mg·min)] | 0.0004 | 0.0002 |
| | $R^2$ | 0.999 | 0.999 |
| 颗粒内扩散模型 | $k_{int1}$[mg/(g·min$^{1/2}$)] | 1.354 | 3.497 |
| | $C_1$(mg/g) | 33.03 | 43.41 |
| | $R_1^2$ | 0.993 | 0.919 |
| | $k_{int2}$[mg/(g·min$^{1/2}$)] | 0.2356 | 0.5721 |
| | $C_2$(mg/g) | 57.71 | 98.08 |
| | $R_2^2$ | 0.892 | 0.828 |

由图 7(d)可知,整个吸附过程可分为 2 个阶段,第一阶段吸附速率较快,对应于表面扩散阶段,此时在静电作用下 Cd(Ⅱ)快速地扩散至吸附剂表面;第二阶段吸附速率较慢,对应于颗粒内扩散和化学反应阶段,此时 Cd(Ⅱ)通过缓慢的颗粒内扩散过程才能与吸附材料内部的吸附位点结合,主要以络合或化学沉淀为主[36].此外,颗粒内扩散模型拟合直线未通过原点,意味着 Zeolite 和 Zeolite@PDA 对 Cd(Ⅱ)的吸附是多种机制共同作用的结果[37].

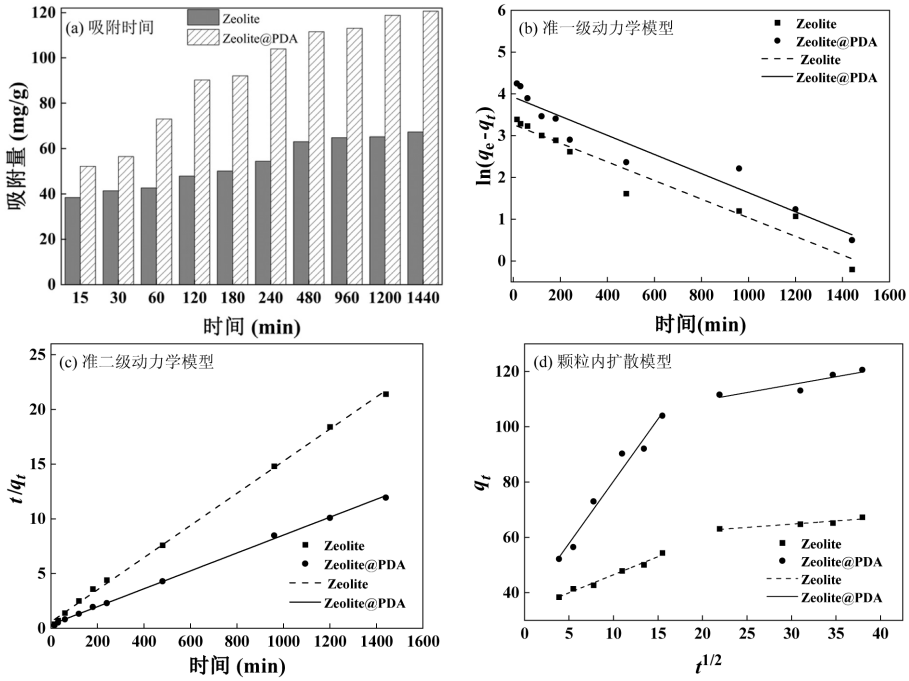



图 7　Zeolite 和 Zeolite@PDA 吸附 Cd(Ⅱ)的动力学模型拟合

Fig.7　Adsorption kinetics of Cd(Ⅱ) by Zeolite and Zeolite@PDA

2.2.5　吸附热力学研究　由表 5 可知,$\Delta G°$均小于 0 且随温度的升高而降低,说明 Zeolite@PDA 吸附 Cd(Ⅱ)是自发的过程,高温有利于吸附的进行;$\Delta H°$为 29.702(kJ/mol)>0,说明该吸附过程是吸热的[38];$\Delta S°$为正值,说明 Zeolite@PDA 吸附 Cd(Ⅱ)前后固液两相界面的紊乱度是增大的[39].

**表 5　Zeolite@PDA 吸附 Cd(Ⅱ)的热力学参数**

Table 5　Thermodynamic parameters of Cd(Ⅱ) adsorption by Zeolite@PDA

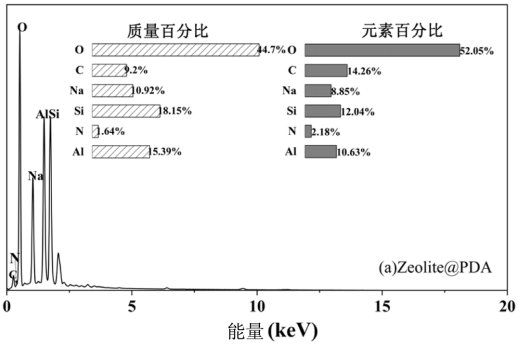
| T(K) | $\Delta H°$(kJ/mol) | $\Delta S°$[J/(mol·K)] | $\Delta G°$(kJ/mol) |
|---|---|---|---|
| 298.15 | | | −2.6019 |
| 303.15 | | | −3.5954 |
| 308.15 | 29.702 | 109.125 | −4.0290 |
| 313.15 | | | −4.5825 |
| 318.15 | | | −4.8136 |

2.2.6　重复利用性能　以 0.1mol/L 的 HCl 溶液为解析剂,经过 3 次吸附−解析过程后,Zeolite@PDA 对 Cd(II)的吸附量仅下降 17%,表明 Zeolite@PDA 具有良好的再生利用性能.

## 2.3　吸附机制

从图 8 中可以看出,吸附后样品中出现代表 Cd 元素的峰,这直接证实 Cd 成功地被 Zeolite@PDA 吸附,同时 Na 元素的峰强度减弱,其含量由 10.92%下降到 0.71%,表明 Zeolite@PDA 吸附过程存在沸石 $Na^+$与 $Cd^{2+}$的离子交换(如下式(6)).

$$(Na^+\text{-Zeolite})+Cd^{2+}\rightarrow(Cd^{2+}\text{-Zeolite})+Na^+ \quad (6)$$



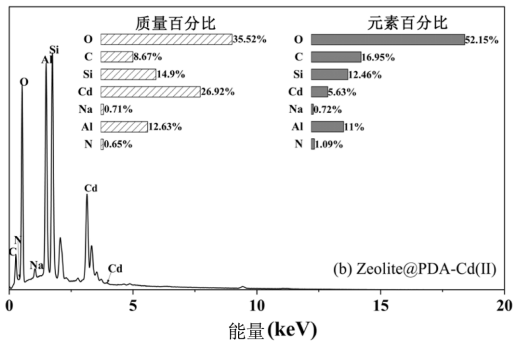
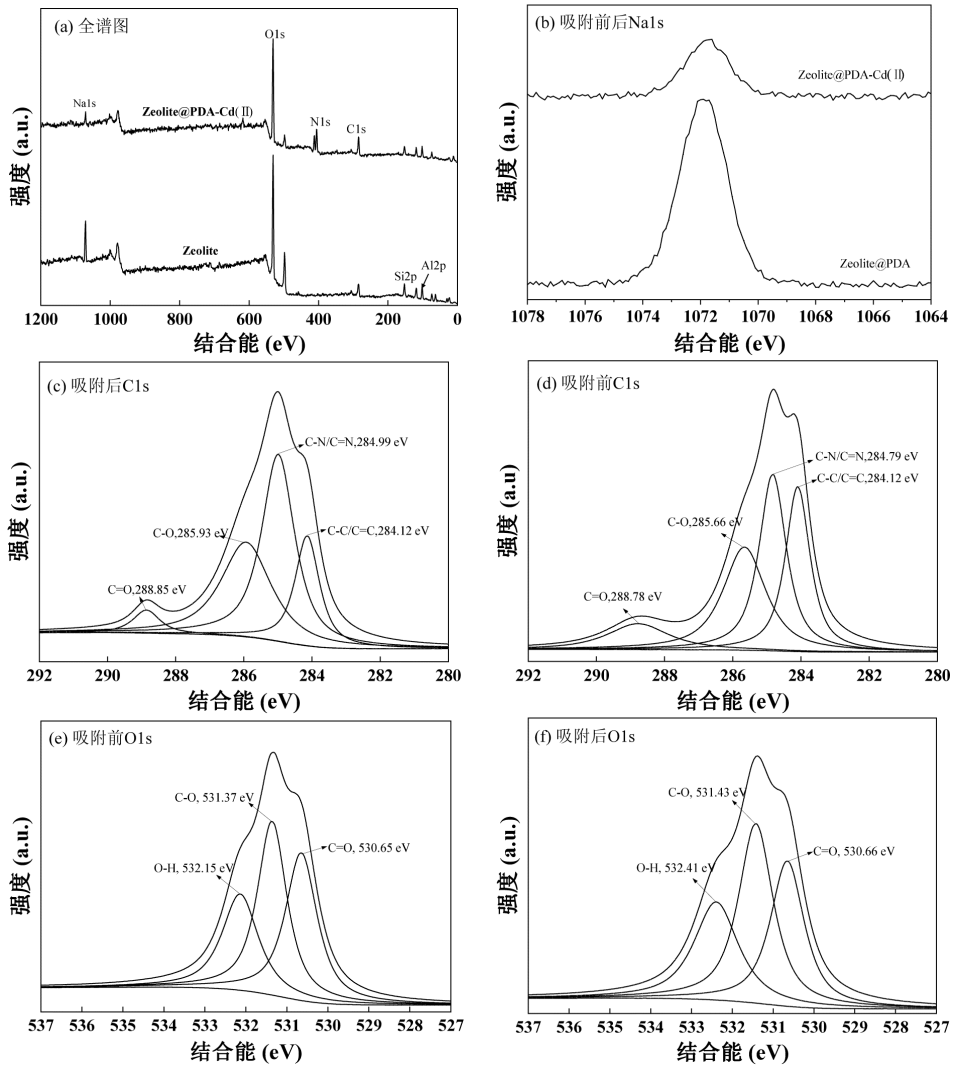



图 8 Zeolite@PDA 和 Zeolite@PDA−Cd(Ⅱ)的 EDS 元素分析

Fig.8 EDS elemental analysis of Zeolite@PDA and Zeolite@PDA−Cd(Ⅱ)

从图 9(a)可以看出,吸附 Cd(Ⅱ)后出现 Cd3d 的吸收峰,且 Na1s 峰强度减弱(图 9(b)),表明 Cd(Ⅱ)通过与 $Na^+$发生离子交换作用而成功地被 Zeolite@PDA 所吸附.由图 9(c)可知,Zeolite@PDA 中 C 原子以 C−C/C=C(284.12eV),C−N/C=N (284.79eV),C−O(285.66eV)和 C=O(288.78eV)官能团形式存在.吸附 Cd(Ⅱ)后,C−N/C=N、C−O 和 C=O 化学键的峰位向更高结合能方向发生偏移,而 C−C/C=C 峰位置保持不变(图 9(d)),表明 C−N/C=N、C−O 和 C=O 与 Cd(Ⅱ)发生了相互作用[40].根据 O1s 的分峰拟合结果(图 9(e)和(f)),Zeolite@PDA 中 C1s 的化学键主要有 C=O(530.65eV) 、 C−O(531.37eV) 和 O−H (532.15eV),吸附 Cd(Ⅱ)后,均向更高结合能偏移,表明 PDA 的邻苯二酚官能团与 Cd(Ⅱ)的络合反应起关键作用[41].同时,Cd3d 的 XPS 图谱在 412.66eV (Cd3d3/2)和 405.67eV(Cd3d5/2)出现双峰现象,这是由于 Cd(Ⅱ)自由离子的价壳层与未配对自旋电子耦合时,光电离形成的内壳层空位耦合了相同价轨道的未配对自旋电子[42],这也说明 Cd(Ⅱ)的吸附与化学反应有关.综上可知,Zeolite@PDA 对 Cd(Ⅱ)的吸附机理包括离子交换和络合反应,见图 10.



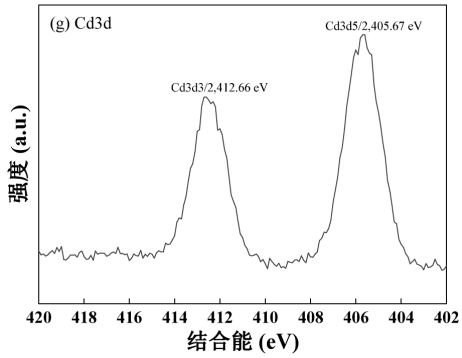



图 9　Zeolite@PDA 和 Zeolite@PDA−Cd(Ⅱ)的 XPS 光谱图

Fig.9　XPS spectra of Zeolite@PDA and Zeolite@PDA−Cd(Ⅱ)

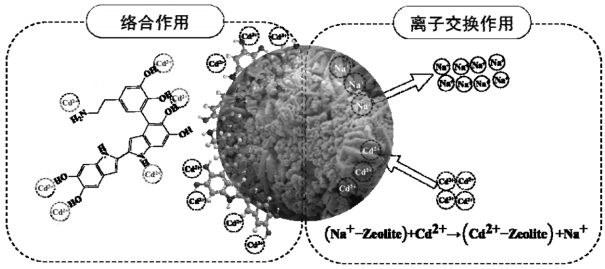



图 10　Zeolite@PDA 吸附 Cd 机理

Fig.10　Mechanism of Cd adsorption on Zeolite@PDA

## 3　结论

3.1　以煤矸石为原料,通过碱熔融−水热法与多巴胺聚合反应成功制备 Zeolite@PDA,聚多巴胺涂层显著提高了矸石基沸石表面有机官能团密度,赋予其对 Cd(Ⅱ)的良好吸附性能,优于大多数文献报道的其他改性方法.

3.2　Zeolite@PDA 对 Cd(Ⅱ)的吸附更符合 Langmuir 模型和准二级动力学模型,说明吸附主要是单分子层的化学吸附.根据 Langmuir 模型计算出,Zeolite@PDA 对 Cd(Ⅱ)的最大吸附容量为 130.89mg/g,远高于矸石基沸石的 66.49mg/g,这说明聚多巴胺改性有利于提高矸石基沸石的吸附性能.

3.3　Zeolite@PDA 对 Cd(Ⅱ)的吸附过程是自发的吸热反应,且伴随着固液界面紊乱度增加.基于元素分析和 XPS 分析结果,推断出 Zeolite@PDA 对 Cd(Ⅱ)的主要吸附机制包括表面络合作用和离子交换.

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