沸石材料在土壤修复工程中的应用研究进展

邓世茂, 楚哲婷, 梁佳欣, 李晶, 陈洪*

南方科技大学环境科学与工程学院, 广东省土壤与地下水污染防治及修复重点实验室, 国家环境保护流域地表水-地下水污染综合防治重点实验室, 深圳 518055

* 联系人, E-mail: chenh3@sustech.edu.cn

2020-06-07 收稿, 2020-07-15 修回, 2020-07-20 接受, 2020-07-22 网络版发表

广东大学生科技创新培育专项资金(pdjh2020c0044)、国家自然科学基金(21777045)和广东省杰出青年基金(2020B151502094)资助

摘要 近年来, 工业的快速发展导致土壤污染成为全球性的环境危机. 土壤污染问题亟待解决, 开发经济、长效的土壤修复材料是关键. 沸石分子筛材料, 由于其优异的离子交换性能和吸附性能, 被广泛应用于土壤修复过程中, 引起环境科学家、材料化学家、土壤学家、矿物学家的广泛关注. 本文基于已被广泛用于土壤修复工程的典型沸石材料, 并着眼于沸石材料的组成与结构, 详细阐述了典型沸石材料的结构与性能之间的对应关系, 综述了沸石材料分别用于不同土壤污染介质修复中的微观作用机理及研究进展.

关键词 沸石材料, 土壤修复, 离子交换, 吸附, 污染物固化

化工工业废弃物的不规范排放、金属矿产资源的开采与加工、石油的泄漏及化肥与农药的滥用, 导致有毒重金属离子、阴离子、有机污染物在土壤中广泛存在, 造成严重的土壤污染问题^[1-4]. 在被污染的土壤中, 80%以上为有毒的无机污染物, 其中最常见的是 Pb^{2+} 、 Cd^{2+} 、 Cr^{3+} 、 Cu^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Zn^{2+} 等重金属离子^[4,5], 以及砷酸盐、铬酸盐、硒酸盐、硫酸盐等有毒阴离子^[6]. 除此之外, 典型有机物如多环芳烃(PAHs)、多氯联苯(PCBs)、有机氯农药(OCPs)、石油等对土壤的污染也不可忽视^[7,8]. 分散在土壤中的污染物, 或影响植物生长, 或经由食物链进入人体, 对人类健康造成巨大危害. 由此可见, 土壤污染的修复治理迫在眉睫.

土壤修复技术通常包括将污染物从土壤中分离去除的“非原位”修复技术和降低污染物迁移率、生物有效性和有害性的“原位”修复技术. “非原位”修复技术主要包括利用酸/碱、螯合剂、表面活性剂、氧化/还原

剂等淋洗液对土壤进行淋洗, 将土壤中的污染物转移到溶液中, 达到污染物去除效果的淋洗法^[9]; 在受污染的土壤中施加直流电场, 使土壤中可流动的污染物通过电渗透、电迁移、电泳的组合机制富集到电极附近, 达到土壤中污染物去除效果的电化学修复法^[10]; 使用高温提取和加工来去除污染土壤中重金属的火法冶金提取技术等^[11]. 这些技术往往存在高能耗、成本较高、易带来二次污染和造成土壤养分严重流失等不足^[12,13]. “原位”修复技术主要包括植物修复法和吸附法, 相较于“非原位”修复方法, 直接将污染物进行“原位”固化修复所需成本更低, 且不存在二次污染^[14]. 其中, 植物修复法能够将赋存于土壤中的污染物有效地提取出来, 产生明显的修复效果, 但是受限于植物生长的周期, 其存在修复周期过长等特点^[15,16]. 吸附法基于材料的表面和结构内部孔道的吸附效应, 简单有效, 被广泛使用. 常用的吸附剂包括活性炭、黏土矿物、生物炭、粉煤灰、磷酸盐等. 前述部分环境吸附材料, 均

引用格式: 邓世茂, 楚哲婷, 梁佳欣, 等. 沸石材料在土壤修复工程中的应用研究进展. 科学通报, 2021, 66: 1002–1013

Deng S M, Chu Z T, Liang J X, et al. Progress of using zeolite materials in soil remediation engineering (in Chinese). Chin Sci Bull, 2021, 66: 1002–1013, doi: [10.1360/TB-2020-0678](https://doi.org/10.1360/TB-2020-0678)

能够被广泛用于土壤修复,并取得一定的修复效果^[17~21]。但是这些吸附剂也还存在明显的不足,比如材料稳定性不佳,吸附效果不够长效等。典型的吸附材料如活性炭材料,其时间一长就容易被微生物分解,导致污染物重新释放到土壤当中^[19]。

近些年,沸石作为一种稳定的吸附材料,由于其优异的离子交换性能、吸附性能,在土壤修复中的应用受到越来越多的关注^[6,22,23]。从化学组成与晶体结构的角度来看,沸石是一种典型的硅铝酸盐, Si-O四面体和 Al-O四面体是构成沸石骨架的初级结构单元;在沸石骨架中,其初级结构单元通过共用氧原子,相互连接形成多元环,构成了沸石骨架的次级结构单元;次级结构单元,通过桥联的氧原子,进一步相互连接,可以形成笼形等不同构型的结构单元;笼形的结构单元通过不同的连接、排列方式进一步形成具有独特孔道拓扑结构和尺寸的沸石骨架结构(图1)^[24]。沸石的骨架中充满着空腔和孔道,最大孔隙率可达到50%,孔道中常吸附有水分子和可交换的阳离子,甚至阴离子^[25]。这些独特的组成和骨架结构使沸石具有良好的阳离子交换容量和表面吸附能力,是一种很好的吸附剂。此外,沸石由于硅铝酸盐构成的骨架具有优异的热稳定性,沸石在被用于土壤修复的过程中,还具有骨架结构稳定、修复效果持久、可适当调节土壤的pH和透气性、对环境友好、无二次污染等优势,对于不同污染物质污染的土壤均有良好的修复效果,具有十分广阔的应用前景^[26]。

基于前人对沸石材料用于土壤修复的详细研究,本文从沸石的组成、结构及其用于土壤污染物修复的性能之间的构效关系出发,全面深入地总结了沸石用于土壤修复过程中的原理、效果及微观作用机制,为开发新型沸石基材料用于复杂土壤修复总结了经验,并对未来开发更加高效的沸石基材料用于土壤修复进

行了系统展望。

1 用于土壤修复的典型沸石材料

1.1 纯沸石材料

1.1.1 天然沸石

目前国际沸石协会(The International Zeolite Association, IZA)共确认了252种沸石结构类型,其中天然沸石结构类型42种(67种天然沸石矿物)。这些天然沸石中只有菱沸石(CHA)、斜发沸石(HEU)、毛沸石(ERI)、镁碱沸石(FER)、钙十字沸石(PHI)、丝光沸石(MOR)和方沸石(ANA)的数量较大且纯度足够高,足以被认为是可开发的自然资源^[27]。其中斜发沸石的储量最为丰富。表1总结了几种储量丰富的天然沸石的组成、结构与性能。总体来说,天然沸石的主要成分为硅铝酸盐、水分子、可交换阳离子,还含有少部分杂质元素。几种常见的天然沸石具有成本低,且与其他类型的吸附剂相比热稳定性和耐酸腐蚀性更好的优势;但是与合成沸石相比,其存在化学组成不一致、纯度低等不足^[28]。沸石的硅铝比,孔径大小,阳离子类型、数量及位置都对其吸附能力有较大影响,可用一定的方法对天然沸石进行调控、改性,进而促进其有效孔道的利用及其离子交换能力的提高。常用的调控处理方法包括离子交换、酸/碱洗和热处理法等^[28]。离子交换处理可以改变沸石骨架中阳离子的类型、位置、数量及孔道开放度,显著提高沸石材料的离子交换容量。酸洗可以去除堵塞孔道的杂质,提高空隙率和吸附能力,但是随着处理强度和持续时间的增加,会逐渐消除骨架结构中的阳离子,最终使结构脱铝;碱洗可以改变沸石的孔径和孔容,但高浓度或长时间的碱洗可能带来沸石骨架的脱硅、脱铝。热处理可以脱去沸石孔道中的水分子,增大孔道开放度和有效孔隙体积。

图1 (网络版彩色)沸石结构。(a)初级结构单元: T-O四面体, T为Si, Al; (b)次级结构单元: 多元环; (c)笼形结构单元; (d)典型FAU沸石的骨架结构

Figure 1 (Color online) Framework structure of zeolite. (a) Primary structural unit: T-O tetrahedron, T is Si or Al; (b) secondary structural unit: Different member rings; (c) cage structural unit; (d) framework structure of FAU type zeolite

表1 几种常见天然沸石的组成、结构与性能

Table 1 Composition, structure, and properties of several natural zeolites

沸石名称	典型的化学组成 ^[29]	Si/Al ^[28]	骨架类型 ^[30]	晶格类型/空间群 ^[30]	主要孔道环数及孔径(Å×Å) ^[30]	孔隙度(%) ^[31]	CEC (meq g ⁻¹) ^[31]
菱沸石(chabazite)	(Ca, Na ₂ , K ₂) ₂ Al ₄ Si ₈ O ₂₄ ·12H ₂ O	1.5~4.0	CHA	三方晶系/ <i>R-3m</i>	8(3.8×3.8)	47	3.84
斜发沸石(clinoptilolite)	(K ₂ , Na ₂ , Ca) ₃ Al ₆ Si ₃₀ O ₇₂ ·21H ₂ O	4.0~5.2	HEU	单斜晶系/ <i>Cm</i>	10(3.1×7.5), 8(3.6×4.6), 8(2.8×4.7)	34	2.16
毛沸石(erionite)	K ₂ (Ca, Na ₂) _{3.5} Al ₉ Si ₂₇ O ₇₂ ·27H ₂ O	3.0~4.0	ERI	六方晶系/ <i>P6₃/mmc</i>	8(3.6×5.1)	35	3.12
镁碱沸石(ferrierite)	(Na ₂ , K ₂ , Ca, Mg) ₃ Al ₆ Si ₃₀ O ₇₂ ·20H ₂ O	4.3~6.2	FER	斜方晶系/ <i>Immm</i>	10(4.2×5.4), 8(3.5×4.8)	28	2.33
钙十字沸石(phillipsite)	K ₂ (Ca, Na ₂) ₂ Al ₆ Si ₁₀ O ₃₂ ·12H ₂ O	1.3~3.4	PHI	单斜晶系/ <i>P2₁/m</i>	8(3.8×3.8), 8(3.0×4.3), 8(3.2×3.3)	31	3.31
丝光沸石(mordenite)	(Na ₂ , Ca) ₄ Al ₈ Si ₄₀ O ₉₆ ·28H ₂ O	4.4~5.5	MOR	斜方晶系/ <i>Cmcm</i>	12(6.5×7.0), 8(2.6×5.7)	28	2.29
方沸石(analcime)	Na ₁₆ Al ₁₆ Si ₃₂ O ₉₆ ·16H ₂ O	- ^{a)}	ANA	立方晶系/ <i>la-3d</i>	高度扭曲的不规则8元环 (4.2×1.6)	18	4.54

a) “-”表示Si/Al不确定

1.1.2 合成沸石

自1948年Barrer^[32]首次合成丝光沸石以来, IZA收录的不同骨架类型的合成沸石已达185种. 沸石的合成方法也越来越丰富, 包括水热合成法^[33]、溶剂热合成法^[34]、干胶转换法^[35]、无溶剂干粉体系合成法^[36]、微波辅助合成法^[37]和蒸汽相体系合成法^[38]. 其中水热合成法的应用最为广泛, 常用的合成原料是一些硅铝化学原料或矿物. 与天然沸石相比, 人工合成可以通过调控原料的硅铝比和合成条件等得到不含杂质、具有特定结构和性质的沸石, 其阳离子交换容量(CEC)往往高于天然沸石^[39]. 虽然合成沸石的性能要显著优于天然沸石, 但成本远高于天然沸石, 限制了其大规模的应用. 为了降低合成沸石的成本, 一方面可以优化合成工艺, 另一方面可以降低原料成本, 通过引入硅铝酸盐废弃物、矿物用于沸石的合成降低其原料成本. 其中, 可用于沸石合成的硅铝酸盐废弃物主要有粉煤灰、生物质灰、赤泥等^[40-42]; 矿物原料包括高岭土、蒙脱石、伊利石、埃洛石等^[43-45]. 合成沸石的类型与原料的硅铝比、活化剂浓度、活化时间、反应温度及固液比均密切相关^[46]. 目前报道的以硅铝酸盐废弃物、矿物为原料合成的沸石已涵盖低硅、中硅和高硅这三类沸石, 其中经验证土壤修复效果较好的主要有A型沸石(LTA)、P型沸石(GIS)和X型沸石(FAU)^[47]. 当然, 基于以粉煤灰等硅铝酸盐废弃物为原料合成的沸石, 其离

子交换容量普遍不及采用商业化学原料合成的沸石. 这主要与工业固废中含有大量重金属杂质有关.

1.2 沸石基复合材料

土壤污染是一个十分复杂的体系, 其污染过程往往是多种不同类型污染物导致的. 与此同时, 土壤修复材料在用于污染物的修复与固化过程中, 由于单一沸石材料的功能单一性, 其往往难以兼顾多种污染物的处理, 以及短期效果与长效稳定性之间的平衡. 在沸石用于土壤修复的过程中, 仅使用单一骨架的沸石作为修复剂, 很大程度上只能修复和固化部分污染物. 为了能够同时有效地固化多种复杂污染物, 达到更好的土壤修复效果, 开发沸石基复合材料十分关键. 目前, 用于土壤修复的沸石基复合材料主要有纳米Fe⁰/沸石复合材料、腐植酸/沸石复合材料和生物炭/沸石复合材料.

1.2.1 纳米Fe⁰/沸石复合材料

近些年, 沸石作为基质材料负载纳米Fe⁰(nZVI)形成的纳米Fe⁰/沸石复合材料(Z-nZVI)在环境修复方面被广泛关注. nZVI具有典型的核-壳结构, Fe⁰为核, 铁氧化合物(FeOOH)为壳(图2(a)), 铁氧化合物壳可以吸附重金属等污染物, 而Fe⁰可以提供电子还原污染物, 是一种兼顾吸附功能和氧化还原功能的多功能环境修复材料, 但是, 由于铁易氧化, 其稳定性差、易发生团聚

图2 (网络版彩色)nZVI的核壳结构(a)和Z-nZVI与污染物相互作用示意图(b)

Figure 2 (Color online) Core-shell structure of nZVI (a) and schematic diagram of the interaction between Z-nZVI and pollutants (b)

现象^[48,49]。利用沸石的大比表面积和高稳定性,以沸石作为基质负载nZVI构筑的Z-nZVI可以有效克服nZVI稳定性差、易团聚的缺点^[50];除此之外,沸石与nZVI的复合还可以进一步弥补沸石对阴离子的亲和能力不足等弱点。基于以上特点,构筑的Z-nZVI复合材料能够与各种污染物通过吸附、氧化/还原、聚集、离子交换、羟基化沉淀、络合等发生相互作用,使得土壤中各种阳离子、阴离子、有机污染物能够得到有效固化^[50]。在此,我们将几种典型的重金属离子/含氧阴离子的固化机理总结于表2,将Z-nZVI与重金属污染物的相互作用示意图总结如图2(b)。

1.2.2 腐植酸/沸石复合材料

腐植酸(HAs)是动植物遗骸经微生物降解、转化等系列生物地球化学过程后得到的一类成分复杂、结构多样的有机酸^[54]。其广泛存在于土壤、天然水体及地质沉积物中,对环境污染物的固化、稳定、迁移、降解有着十分重要的意义。HAs由芳环及多种官能团构成(图3(a)),其表面的众多官能团可以有效地固化阳离子,高电荷密度、半径小的“硬离子”主要与 $-\text{COO}^-$ 、 $-\text{O}^-$ 通过静电力相互作用而固化;而低电荷密度、半径大的“软离子”则主要是与HAs的酸性官能团,尤其是 $-\text{COOH}$ 形成共价配位键; Cu^{2+} 、 Fe^{2+} 、 Co^{2+} 、 Zn^{2+} 、 Pb^{2+} 、 Ni^{2+} 等离子则是介于“硬离子”与“软离子”之间,因此,其与腐植酸同时存在静电相互作用和络合作用^[55,56]。HAs是一种两亲分子,由拉长的疏水部分和尾部的一个或多个阴离子基团组成,其可以通过自组装,形成类似胶束的结构(图3(b)),称为假胶束^[57]。形成的假胶束疏水端朝内,亲水端朝外,非极性有机物可以固定在假胶束的疏水端中心。HAs具有一定的土壤修复能力,但是与沸石结合使用后,其效果好于单独使用HAs

或者沸石。Shi等人^[58]报道的沸石与HAs联合修复 Pb^{2+} 污染的花园土表明,沸石与HAs的结合使用可以更高效地降低土壤中生物有效Pb形态的百分含量,不可提取或者是有机结合的无效Pb形态百分比增加。Dercová等人^[59]报道HAs与斜发沸石结合形成的有机矿物络合物(OMC)用于吸附土壤中的五氯苯酚(PCP),吸附效果好于单独的沸石或者HAs。虽然陆续有沸石与HAs的联合使用的相关报道,但是HAs与沸石的协同机制尚不清楚,需要进一步研究。

1.2.3 生物炭/沸石复合材料

生物炭是指有机生物质在低氧条件下通过热解或气化而形成的含碳固体,其比表面积大、表面官能团丰富、具有很好的吸附性能,且来源广泛、成本低廉,是一种很有前景的土壤修复材料^[60,61]。生物炭对无机重金属离子和有机污染物均有较好的固化作用,其相互作用示意图总结如图4所示。对于重金属离子,其主要与生物炭通过静电相互作用、离子交换、表面络合、沉淀等相互作用被直接吸附固化;也可通过改变土壤的pH、矿物质组成及有机碳含量,促进土壤对重金属离子的吸附,从而间接固化重金属离子^[19]。有机污染物的固化主要以分配作用、吸附作用和空隙填充为主^[62]。生物炭虽然有很好的吸附效果,但是存在结构不是很稳定、长期效应不佳^[63]、与有机物间的结合力太强导致降低农药药效等不足^[19]。通过构筑生物炭/沸石复合材料(BZ),可以有效提高生物炭材料的稳定性,对因与有机物结合太强带来的副作用也有一定的缓解作用。Ahmad等人^[64]将斜发沸石加入到椰枣树废料中热解,得到的BZ是一种有机-矿物复合物,BZ中可能形成了Si-C键,其结构组成与物理、化学性质均与单纯的生物炭材料不同,稳定性显著高于单纯的生物炭材料。

表 2 几种污染物与Z-nZVI相互作用的机理

Table 2 Mechanisms of Z-nZVI interacting with several pollutants

基质材料	目标污染物	相互作用机理	文献
β沸石	Sb(Ⅲ)	第一步: Sb(Ⅲ)被吸附到Z-nZVI表面, 然后立即被还原为Sb(0), 同时nZVI被氧化; 第二步: Fe(0)及其氧化物不断演化, 氧化程度提高, 吸附的Sb(0)被铁氧化合物包裹, 固定在沸石表面	[51]
斜发沸石	As(Ⅲ)	As(Ⅲ)先被氧化为As(V), 然后再与Z-nZVI表面的铁氧化合物络合, 固定在其外壳上 $\text{Fe}^0 + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2$ $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^\cdot$ $\text{HAsO}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{AsO}_4^{2-} + \text{H}^+$ $\text{Zeolite-FeOH} + \text{H}_2\text{AsO}_4^{2-} \rightarrow \text{Zeolite-FeO-(AsO(OH)}_2)_2 + \text{OH}^-$	[52]
斜发沸石	Cd(Ⅱ)	Cd(Ⅱ)与nZVI的共沉淀吸附占主导作用, 同时沸石也能吸附Cd(Ⅱ) $x\text{Cd}^{2+} + (1-x)\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Cd}_x\text{Fe}_{(1-x)}(\text{OH})_2$	[52]
斜发沸石	Pb(Ⅱ)	nZVI对Pb(Ⅱ)的还原占主导作用, 同时沸石也能吸附Pb(Ⅱ) $\text{Pb}^{2+} + \text{Fe}^0 + 2\text{OH}^- \rightarrow \text{Pb}^0 + \text{Fe}(\text{OH})_2$	[52]
斜发沸石	As(V)	在酸性条件下, As(V)以 H_2AsO_4^- 的形态存在, 与FeOOH络合形成 FeAsO_4 ; $\text{FeOOH} + \text{H}_2\text{AsO}_4^- + \text{H}^+ \rightarrow \text{FeAsO}_4 + 2\text{H}_2\text{O}^-$ 碱性条件下, As以 HAsO_4^{2-} 的形态存在, 与铁氧化合物及Pb(Ⅱ)的水合物形成B型三元络合物 $\text{Zeolite-FeOH} + \text{HAsO}_4^{2-} + [\text{Pb}(\text{OH})]^\cdot \rightarrow \text{Zeolite-PbFe}(\text{HAsO}_4)\text{OH} + \text{OH}^-$	[53]

Mosa等人^[65]研究了水葫芦与天然沸石热解得到的BZ, 脱附性优于单纯的生物炭材料, 说明BZ与污染物间的结合较纯生物炭弱. 同时, 生物炭与沸石的复合对沸石性能的提升也有促进作用. 沸石的孔径与分子大小相近, 吸附质(尤其是尺寸较大的分子或离子)在沸石孔道中的扩散较差, 导致可利用的沸石内表面积和体积利用不足, 限制了沸石的性能. Kumar Awasthi等人^[66]以枣核源炭材料为支架, X型沸石在其表面生长得到一种含有微孔和介孔/大孔的分级多孔复合材料, 介孔和大孔可以促进吸附质进入沸石微孔中的活性位点, 减小扩散阻力. 此外, 将生物炭与沸石材料简单的联合使用, 修复效果也优于单一的材料. Boostani等人^[67]研究表明, 往土壤中单独添加天然沸石或生物炭对Cd的固化都有一定效果, 但是效果最好的是3%的羊粪源生物炭+6%天然沸石联合使用. 沸石的表面积和孔径大小不如生物炭, 但是稳定性更好; 生物炭的表面积大、表

面官能团丰富、孔径大, 但是稳定性稍差. 沸石与生物炭复合后, 优势互补, 得到的生物炭/沸石复合材料是一种很有潜力的土壤修复材料.

2 沸石材料在不同污染物类型土壤修复中的应用

2.1 无机阳离子污染修复

土壤中无机阳离子污染物通常是指 Pb^{2+} 、 Cd^{2+} 、 Cr^{3+} 、 Cu^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Zn^{2+} 等重金属离子. 这些重金属离子往往难以降解, 造成的影响持久, 而且容易在环境中随着水、气迁移, 因而, 容易进一步污染植物或者是自然水体. 沸石的大比表面积和阳离子交换容量非常有利于固化重金属离子, 被广泛应用于重金属污染的土壤修复^[6]. Lahori等人^[26]在土壤中添加沸石后, 发现沸石能够有效固化土壤中的 Pb^{2+} 、 Cd^{2+} , 对种植的

图 3 (网络版彩色)腐植酸单体的结构模型(a)和腐植酸假胶束模型(b)
Figure 3 (Color online) Model of the HAS monomer (a) and HAS pseudo micelles (b)

图4 (网络版彩色)生物炭与重金属离子及有机物的相互作用示意图
Figure 4 (Color online) Schematic diagram of the interaction between biochar and heavy metal ions and organic compounds

甘蓝及玉米的生长都有促进作用。Lee等人^[68]在 Cu^{2+} 和 Zn^{2+} 污染的稻田中添加斜发沸石和粉煤灰后,发现两者均对 Cu^{2+} 和 Zn^{2+} 有固化作用,其中沸石的效果更好,但是对水稻生物量的增加并无帮助。Li等人^[69]在 Pb^{2+} 污染的花园土中添加天然沸石(主要包含斜发沸石和片沸石(HEU))后,降低了植物对 Pb^{2+} 的吸收。Zhao等人^[70]将用粉煤灰合成的沸石添加到稻田中后,显著降低了 Cd^{2+} 的生物有效性,促进了水稻的生长。沸石材料对污染土壤的修复主要是通过固化土壤中的重金属离子,抑制其在土壤中的迁移和降低生物有效性,作用过程及反应机理总结如下^[23]: (1) 利用沸石的碱性多孔硅铝酸盐特性,通过加入沸石碱化土壤,使得土壤中pH升高,重金属离子以碳酸盐或者是氢氧化物的形式沉淀下来; (2) 土壤的碱化可以促进重金属离子在土壤中矿物表面的络合吸附; (3) 沸石通过离子交换和吸附,将重金属离子固定在沸石的孔道内,使得重金属离子稳定存在于沸石结构内部。通常,低硅铝比、大孔径沸石更有利于固化重金属离子,这类沸石一般有A型沸石、P型沸石和X型沸石。

除了重金属离子污染,核素离子的泄漏也会对土壤造成长期的、严重的危害。沸石也被广泛用于放射性核素的固化,以阻止核素污染的扩散^[71]。天然沸石与有机树脂相比,对放射性核素(^{90}Sr 、 ^{137}Cs 、 ^{60}Co 、 ^{45}Ca 、 ^{51}Cr 等)具有很高的选择性,且成本更低、更能抵抗核降解,是一种有效的核污染修复材料^[31]。

2.2 无机阴离子污染修复

无机阴离子污染物主要是砷酸盐、铬酸盐、硒酸

盐、硫酸盐、高氯酸盐、铋酸盐等含氧阴离子。阴离子与沸石骨架所带的负电荷相斥,使得阴离子难以吸附在沸石表面,传统的沸石材料用于土壤中阴离子污染物的修复研究很少,但是随着沸石基复合材料的出现,沸石材料用于土壤阴离子的修复渐渐开始受到关注。目前,能够用于土壤中阴离子污染物固化的沸石基复合材料主要是Z-nZVI。Li等人^[52]在2018年报道的以斜发沸石为基质制备的Z-nZVI可以有效固化土壤和水中的 Cd^{2+} 、 Pb^{2+} 和砷酸盐($\text{As}(\text{III})$)。在此基础上,Li等人^[53]在2020年进一步报道了Z-nZVI分别对酸性和碱性农田土壤中 Cd^{2+} 、 Pb^{2+} 和砷酸盐($\text{As}(\text{V})$)的固化,并提出在酸性土壤中,As主要以 H_2AsO_4^- 的形态存在,易与 FeOOH 络合形成 FeAsO_4 ;而在碱性土壤中,As主要以 HAsO_4^{2-} 的形态存在,易与铁氧化物及 Pb^{2+} 的水合离子形成B型三元络合物(反应式见表2)。在纳米 Fe^0 /沸石复合材料体系中,阴离子主要被nZVI固化,沸石主要起分散nZVI的作用。

此外,采用十六烷基三甲基铵(HDTMA)等表面活性剂对沸石的外表面进行修饰,沸石表面的负电荷被中和后,其也可以吸附阴离子^[72~74]。表面活性剂浓度(C)大于临界胶束浓度(CMC)时,在沸石表面形成双分子层胶束,阴离子可与沸石表面双分子层胶束的阳离子头部通过静电相互作用吸附在沸石表面,成为钝化态(图5)^[72]。但是,表面活性剂修饰改性的沸石材料的环境修复应用主要集中在水污染治理方面,鲜有土壤修复方面的研究报道,是否适合于土壤中阴离子污染物的固化还需进一步研究证实。

2.3 有机物污染修复

农药和化肥的不合理使用,石油的泄漏,医药及染料行业废弃物的不规范排放是土壤有机污染的主要源头^[4,75]。对于这些污染物,吸附剂固化是一种常用的方法,常用的吸附剂是活性炭和生物炭^[7],沸石也常被用于有机物污染的土壤修复。Rehakova等人^[76]在多氯联苯(PCB)污染的土壤中添加天然斜发沸石后,植物中PCB的浓度由4765降至2524 $\mu\text{g}/\text{kg}$ 。Petrovic等人^[77]在砂质土中添加富含斜发沸石的材料后,有效降低了甲灵霜(*D,L-N*-(2,6-二甲基苯基)-*N*-(2-甲氧基乙酰)丙氨酸甲酯)向地下水中的迁移。Bandura等人^[78]研究表明,合成的Na-P1和Na-X型沸石处理石油污染的土壤的效果好于商用吸附剂“Abodan”。沸石固化有机物的机理主要是通过范德华力将有机物吸附在孔道中;此外,沸石

图 5 阴离子在表面修饰的沸石表面的吸附示意图

Figure 5 Schematic diagram of anions adsorbed on surfactant-modified zeolite surface

孔道中特定的吸附位点(氧位点和酸位点)与有机物间的酸碱相互作用及氢键也有部分贡献^[79]。影响沸石吸附有机物性能的主要因素是其孔道结构和孔道疏水性。

沸石孔道的孔径越大、腔体体积越大, 其对有机

物的吸附性能也就越好。FAU型沸石对硝基苯的吸附能力高于BEA、MFI和MOR型沸石, BEA对苯酚、二氯苯酚和硝基苯的吸附能力高于MOR, 有关FAU、BEA、MFI、MOR的主要孔道结构信息总结于表3^[79]。

表 3 FAU、BEA、MFI、MOR四种骨架沸石的孔道结构

Table 3 Channel structure of zeolites FAU, BEA, MFI, and MOR

骨架类型	骨架结构	主要孔道环数及孔径($\text{\AA} \times \text{\AA}$)	有效比表面积(m^2/g)	文献
FAU		12(7.4×7.4)	1211.42	[79]
BEA		12(6.6×6.7) 12(5.6×5.6)	1220.45	[79]
MFI		10(5.1×5.5) 10(5.3×5.6)	834.41	[79]
MOR		12(6.5×7.4) 8(2.6×5.7)	1010.22	[79]

图6 (网络版彩色)水分子在沸石孔道中的吸附。(a) 亲水孔道中, 水分子通过配位相互作用和氢键作用, 在孔壁表面的亲水中心周围排列并保持固定位置; (b) 疏水孔道中, 水分子与疏水表面相互作用较弱, 水分子通过有限的分子间氢键作用形成无序的团簇

Figure 6 (Color online) Absorption of water molecules in a zeolite micropore. (a) In hydrophilic pore, water molecules arrange around the hydrophilic centre on the pore wall surface and stay a fixed position, through coordination interaction and hydrogen-bond; (b) in hydrophobic pore, interaction between water molecules and hydrophobic surfaces is weak, and water molecules form disordered clusters through limited intermolecular hydrogen-bond

Bandura等人^[78]研究表明, 石油主要通过物理吸附填充在沸石的空腔中和覆盖在沸石外表面, 石油中的有机分子的尺寸大于微孔, 只能进入介孔, 所以沸石对石油污染物的吸附能力与其骨架结构中介孔比例的大小正相关。Muir和Bajda^[75]研究的季铵盐修饰后的Na-P1沸石对石油的吸附也表明沸石骨架结构中的介孔是控制吸附性能的主要因素。

此外, 有机物往往与水共存, 在利用沸石吸附有机物的过程中, 有机物与水之间存在竞争吸附。沸石孔道越疏水, 吸附有机物的能力越强。沸石孔道的疏水性受其孔道表面的亲水中心(表面阳离子与表面硅羟基)密度控制, 密度越低, 越疏水。亲水中心的密度主要取决于Si/Al, Al含量越低, 阳离子含量越低; 同时脱Al过程中, 相邻的硅羟基发生交叉缩合形成非极性、疏水的硅氧烷表面。在亲水孔道中, 水分子通过与硅羟基形成氢键、与阳离子形成配位共价键吸附, 形成“沸石水”(zeolitic water)(图6(a))。在疏水性孔道中, 缺少配位共价键和氢键强相互作用, 水分子通过毛细凝聚填充在孔道中, 形成“游离态”水(“loosely bound” water)(图6(b))。“游离态”水与孔道表面的相互作用弱, 与疏水孔道间的相互作用的能量约为2.5 kJ/mol, 而有机物与疏水孔道的范德华相互作用的能量可高达4 kJ/mol, 所以在疏水孔道中, 有机物很容易取代水分子吸附在沸石上^[80]。此外, 调节沸石骨架中的硅铝比可以有效改变沸石的疏水性, 表面活化剂修饰改性也可以改变沸石表面的疏水性^[81~84]。

总的来说, 在不存在水分或者只含有少量水分的情况下, 沸石对有机物的吸附主要取决于孔道结构, 孔

道孔径越大, 越有利于有机物的吸附。但是, 根据紧密配合理论, 当沸石孔径与有机分子尺寸相当时, 吸附效果最好^[85]。若环境中含有较多水分时, 需要同时考虑沸石的孔道结构和疏水性。通常, 高硅铝比、大孔径沸石有利于有机物的吸附。

3 总结与展望

综上所述, 沸石具有比表面积大、阳离子交换容量大、化学稳定性好、机械强度高且廉价易得的特点, 是一种很有前景的土壤修复材料。虽然沸石材料在土壤修复中的应用较多, 但是其在用于不同类型污染物的土壤修复过程中, 其修复机理、影响因素都还不是很明显, 存在争议。此外, 沸石材料在阳离子吸附方面的研究已经很多, 但在阴离子和有机物吸附方面, 相关的研究、应用还比较欠缺。深入系统研究沸石对土壤中不同类型污染物的修复效果、影响因素, 从原子级尺度揭示沸石材料在土壤修复中的构效关系及修复机理, 构建沸石材料在土壤修复应用过程中的完整的认知科学体系, 是未来科学发展的必然。

此外, 从成本角度考虑, 人工合成虽然可以对沸石的组成、结构进行深入的调控, 使其拥有定向功能化性质, 赋予其与天然沸石相比, 更加优异的环境修复功能。但是其成本较高, 难以大规模应用, 若能降低沸石的合成成本, 将大大促进沸石材料在土壤修复中的应用。再次, 沸石与其他土壤修复材料复合, 得到的复合材料也显现出了很好的修复效果, 具有很好的应用前景, 但是大多数情况下, 沸石与复合材料中其他组分间的协同机制尚不清楚, 亟须进一步研究揭示。

参考文献

- 1 Li P, Wang X, Allinson G, et al. Risk assessment of heavy metals in soil previously irrigated with industrial wastewater in Shenyang, China. *J Hazard Mater*, 2009, 161: 516–521
- 2 Khalid S, Shahid M, Niazi N K, et al. A comparison of technologies for remediation of heavy metal contaminated soils. *J Geochem Explor*, 2017, 182: 247–268
- 3 Wei Z, Wang J J, Gaston L A, et al. Remediation of crude oil-contaminated coastal marsh soil: Integrated effect of biochar, rhamnolipid biosurfactant and nitrogen application. *J Hazard Mater*, 2020, 396: 122595
- 4 Chen R, de Sherbinin A, Ye C, et al. China's soil pollution: Farms on the frontline. *Science*, 2014, 344: 691
- 5 Feng W, Zhang S, Zhong Q, et al. Soil washing remediation of heavy metal from contaminated soil with EDTMP and PAA: Properties, optimization, and risk assessment. *J Hazard Mater*, 2020, 381: 120997
- 6 Misaelides P. Application of natural zeolites in environmental remediation: A short review. *Microporous Mesoporous Mater*, 2011, 144: 15–18
- 7 Kołtowski M, Hilber I, Bucheli T D, et al. Effect of activated carbon and biochars on the bioavailability of polycyclic aromatic hydrocarbons in different industrially contaminated soils. *Environ Sci Pollut Res*, 2016, 23: 11058–11068
- 8 Zhang X, Wang H, He L, et al. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environ Sci Pollut Res*, 2013, 20: 8472–8483
- 9 Dermont G, Bergeron M, Mercier G, et al. Soil washing for metal removal: A review of physical/chemical technologies and field applications. *J Hazard Mater*, 2008, 152: 1–31
- 10 Yeung A T, Gu Y Y. A review on techniques to enhance electrochemical remediation of contaminated soils. *J Hazard Mater*, 2011, 195: 11–29
- 11 Evanko C R, Dzombak D A. Remediation of Metals-Contaminated Soils and Groundwater. Pittsburgh: Ground-Water Remediation Technologies Analysis Center, 1997
- 12 Xu J, Liu C, Hsu P C, et al. Remediation of heavy metal contaminated soil by asymmetrical alternating current electrochemistry. *Nat Commun*, 2019, 10: 2440
- 13 Nair R R, Russel J G, Pradeep S, et al. A novel *ex-situ* bio-remediation process for perchlorate contaminated soil. *Chemosphere*, 2020, 247: 125947
- 14 Abdullahi M S. Soil contamination, remediation and plants: Prospects and challenges. In: Hakeem K R, Sabir M, Öztürk M, et al., eds. *Soil Remediation and Plants*. New York: Academic Press, 2015. 525–546
- 15 Salt D E, Blaylock M, Kumar N P B A, et al. Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. *Nat Biotechnol*, 1995, 13: 468–474
- 16 Saravanan A, Jeevanantham S, Narayanan V A, et al. Rhizoremediation—A promising tool for the removal of soil contaminants: A review. *J Environ Chem Eng*, 2020, 8: 103543
- 17 Liu X, Yu G. Combined effect of microwave and activated carbon on the remediation of polychlorinated biphenyl-contaminated soil. *Chemosphere*, 2006, 63: 228–235
- 18 Xu Y, Liang X, Xu Y, et al. Remediation of heavy metal-polluted agricultural soils using clay minerals: A review. *Pedosphere*, 2017, 27: 193–204
- 19 He L, Zhong H, Liu G, et al. Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China. *Environ Pollut*, 2019, 252: 846–855
- 20 Zha F, Ji C, Xu L, et al. Assessment of strength and leaching characteristics of heavy metal-contaminated soils solidified/stabilized by cement/fly ash. *Environ Sci Pollut Res*, 2019, 26: 30206–30219
- 21 Zeng G, Wan J, Huang D, et al. Precipitation, adsorption and rhizosphere effect: The mechanisms for phosphate-induced Pb immobilization in soils—A review. *J Hazard Mater*, 2017, 339: 354–367
- 22 Colella C. Recent advances in natural zeolite applications based on external surface interaction with cations and molecules. In: Xu R R, Gao Z, Chen J S, et al., eds. *Studies in Surface Science and Catalysis*. Berlin: Elsevier, 2007. 2063–2073
- 23 Shi W, Shao H, Li H, et al. Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *J Hazard Mater*, 2009, 170: 1–6
- 24 Zeng S J. Synthesis of zeolites and hierarchically porous materials (in Chinese). Doctor Dissertation. Changchun: Jilin University, 2016 [曾尚景. 绿色合成沸石分子筛及多级孔材料. 博士学位论文. 长春: 吉林大学, 2016]
- 25 Kesraoui-Ouki S, Cheeseman C R, Perry R. Natural zeolite utilisation in pollution control: A review of applications to metals' effluents. *J Chem Technol Biotechnol*, 1994, 59: 121–126
- 26 Lahori A H, Mierzwa-Hersztek M, Demiraj E, et al. Direct and residual impacts of zeolite on the remediation of harmful elements in multiple contaminated soils using cabbage in rotation with corn. *Chemosphere*, 2020, 250: 126317
- 27 Eroglu N, Emekci M, Athanassiou C G. Applications of natural zeolites on agriculture and food production. *J Sci Food Agric*, 2017, 97: 3487–3499
- 28 Ackley M. Application of natural zeolites in the purification and separation of gases. *Microporous Mesoporous Mater*, 2003, 61: 25–42

- 29 Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem Eng J*, 2010, 156: 11–24
- 30 Baerlocher C, McCusker L B, Olson D H. Atlas of Zeolite Framework Types. Amsterdam: Elsevier, 2007
- 31 Mumpton F A. La roca magica: Uses of natural zeolites in agriculture and industry. *Proc Natl Acad Sci USA*, 1999, 96: 3463–3470
- 32 Barrer R M. Syntheses and reactions of mordenite. *J Chem Soc*, 1948, 24: 2158–2163
- 33 Healey A M, Johnson G M, Weller M T. The synthesis and characterisation of JBW-type zeolites. *Microporous Mesoporous Mater*, 2000, 37: 153–163
- 34 Kessler H. Synthesis of high-silica zeolites and phosphate-based materials in the presence of fluoride. In: Robson H, Lillerud K P, eds. *Verified Syntheses of Zeolitic Materials*. Amsterdam: Elsevier, 2001. 25–26
- 35 Chen B, Huang Y. ^{17}O solid-state NMR spectroscopic studies of the involvement of water vapor in molecular sieve formation by dry-gel conversion. *J Am Chem Soc*, 2006, 128: 6437–6446
- 36 Ren L, Wu Q, Yang C, et al. Solvent-free synthesis of zeolites from solid raw materials. *J Am Chem Soc*, 2012, 134: 15173–15176
- 37 Zeng S, Wang R, Zhang Z, et al. Solventless green synthesis of sodalite zeolite using diatomite as silica source by a microwave heating technique. *Inorg Chem Commun*, 2016, 70: 168–171
- 38 Kasneryk V, Shamzyk M, Zhou J, et al. Vapour-phase-transport rearrangement technique for the synthesis of new zeolites. *Nat Commun*, 2019, 10: 5129
- 39 Querol X, Alastuey A, Moreno N, et al. Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash. *Chemosphere*, 2006, 62: 171–180
- 40 Murayama N, Yamamoto H, Shibata J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *Int J Miner Process*, 2002, 64: 1–17
- 41 Yoldi M, Fuentes-Ordoñez E G, Korili S A, et al. Zeolite synthesis from industrial wastes. *Microporous Mesoporous Mater*, 2019, 287: 183–191
- 42 Xie W M, Zhou F P, Bi X L, et al. Accelerated crystallization of magnetic 4A-zeolite synthesized from red mud for application in removal of mixed heavy metal ions. *J Hazard Mater*, 2018, 358: 441–449
- 43 Zayed A M, Selim A Q, Mohamed E A, et al. Adsorption characteristics of Na-A zeolites synthesized from Egyptian kaolinite for manganese in aqueous solutions: Response surface modeling and optimization. *Appl Clay Sci*, 2017, 140: 17–24
- 44 Belviso C, Cavalcante F, Niceforo G, et al. Sodalite, faujasite and A-type zeolite from 2:1 dioctahedral and 2:1:1 trioctahedral clay minerals. A singular review of synthesis methods through laboratory trials at a low incubation temperature. *Powder Technol*, 2017, 320: 483–497
- 45 Meng Q, Chen H, Lin J, et al. Zeolite A synthesized from alkaline assisted pre-activated halloysite for efficient heavy metal removal in polluted river water and industrial wastewater. *J Environ Sci*, 2017, 56: 254–262
- 46 Ren X, Xiao L, Qu R, et al. Synthesis and characterization of a single phase zeolite A using coal fly ash. *RSC Adv*, 2018, 8: 42200–42209
- 47 Querol X, Moreno N, Umaña J C, et al. Synthesis of zeolites from coal fly ash: An overview. *Int J Coal Geol*, 2002, 50: 413–423
- 48 Chen Z, Wei D, Li Q, et al. Macroscopic and microscopic investigation of Cr(VI) immobilization by nanoscaled zero-valent iron supported zeolite MCM-41 via batch, visual, XPS and EXAFS techniques. *J Clean Prod*, 2018, 181: 745–752
- 49 Wang S, Zhao M, Zhou M, et al. Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water: A critical review. *J Hazard Mater*, 2019, 373: 820–834
- 50 Zou Y, Wang X, Khan A, et al. Environmental remediation and application of nanoscale zero-valent iron and its composites for the removal of heavy metal ions: A review. *Environ Sci Technol*, 2016, 50: 7290–7304
- 51 Zhou Z, Dai C, Zhou X, et al. The removal of antimony by novel NZVI-zeolite: The role of iron transformation. *Water Air Soil Pollut*, 2015, 226: 76
- 52 Li Z, Wang L, Meng J, et al. Zeolite-supported nanoscale zero-valent iron: New findings on simultaneous adsorption of Cd(II), Pb(II), and As(III) in aqueous solution and soil. *J Hazard Mater*, 2018, 344: 1–11
- 53 Li Z, Wang L, Wu J, et al. Zeolite-supported nanoscale zero-valent iron for immobilization of cadmium, lead, and arsenic in farmland soils: Encapsulation mechanisms and indigenous microbial responses. *Environ Pollut*, 2020, 260: 114098
- 54 MacCarthy P. 7 The principles of humic substances: An introduction to the first principle. In: Ghabbour E A, Davies G, eds. *Humic Substances: Structures, Models and Functions*. Cambridge: the Royal Society of Chemistry, 2001. 19–30
- 55 Soler-Rovira P, Madejón E, Madejón P, et al. *In situ* remediation of metal-contaminated soils with organic amendments: Role of humic acids in copper bioavailability. *Chemosphere*, 2010, 79: 844–849
- 56 von Wandruszka R. Humic acids: Their detergent qualities and potential uses in pollution remediation. *Geochem Trans*, 2000, 1: 10–15
- 57 de Melo B A G, Motta F L, Santana M H A. Humic acids: Structural properties and multiple functionalities for novel technological developments. *Mater Sci Eng C*, 2016, 62: 967–974
- 58 Shi W, Shao H, Li H, et al. Co-remediation of the lead-polluted garden soil by exogenous natural zeolite and humic acids. *J Hazard Mater*, 2009, 167: 136–140

- 59 Dercová K, Sejáková Z, Skokanová M, et al. Bioremediation of soil contaminated with pentachlorophenol (PCP) using humic acids bound on zeolite. *Chemosphere*, 2007, 66: 783–790
- 60 Gu J F, Zhou H, Yang W T, et al. Effects of an additive (hydroxyapatite-biochar-zeolite) on the chemical speciation of Cd and As in paddy soils and their accumulation and translocation in rice plants. *Environ Sci Pollut Res*, 2018, 25: 8608–8619
- 61 Ahmad M, Usman A R A, Rafique M I, et al. Engineered biochar composites with zeolite, silica, and nano-zerovalent iron for the efficient scavenging of chlortetracycline from aqueous solutions. *Environ Sci Pollut Res*, 2019, 26: 15136–15152
- 62 Wu S, He H, Inthapanya X, et al. Role of biochar on composting of organic wastes and remediation of contaminated soils—A review. *Environ Sci Pollut Res*, 2017, 24: 16560–16577
- 63 Li Y, Liu X, Wu X, et al. Effects of biochars on the fate of acetochlor in soil and on its uptake in maize seedling. *Environ Pollut*, 2018, 241: 710–719
- 64 Ahmad M, Ahmad M, Usman A R A, et al. Date palm waste-derived biochar composites with silica and zeolite: Synthesis, characterization and implication for carbon stability and recalcitrant potential. *Environ Geochem Health*, 2019, 41: 1687–1704
- 65 Mosa A, El-Ghamry A, Tolba M. Biochar-supported natural zeolite composite for recovery and reuse of aqueous phosphate and humate: Batch sorption-desorption and bioassay investigations. *Environ Technol Innov*, 2020, 19: 100807
- 66 Kumar Awasthi M, Wang M, Pandey A, et al. Heterogeneity of zeolite combined with biochar properties as a function of sewage sludge composting and production of nutrient-rich compost. *Waste Manage*, 2017, 68: 760–773
- 67 Boostani H R, Hardie A G, Najafi-Ghiri M, et al. Investigation of cadmium immobilization in a contaminated calcareous soil as influenced by biochars and natural zeolite application. *Int J Environ Sci Technol*, 2018, 15: 2433–2446
- 68 Lee D S, Lim S S, Park H J, et al. Fly ash and zeolite decrease metal uptake but do not improve rice growth in paddy soils contaminated with Cu and Zn. *Environ Int*, 2019, 129: 551–564
- 69 Li H, Shi W, Shao H, et al. The remediation of the lead-polluted garden soil by natural zeolite. *J Hazard Mater*, 2009, 169: 1106–1111
- 70 Zhao H, Huang X, Liu F, et al. A two-year field study of using a new material for remediation of cadmium contaminated paddy soil. *Environ Pollut*, 2020, 263: 114614
- 71 Munthali M W, Johan E, Aono H, et al. Cs⁺ and Sr²⁺ adsorption selectivity of zeolites in relation to radioactive decontamination. *J Asian Ceram Soc*, 2015, 3: 245–250
- 72 Reeve P J, Fallowfield H J. Natural and surfactant modified zeolites: A review of their applications for water remediation with a focus on surfactant desorption and toxicity towards microorganisms. *J Environ Manage*, 2018, 205: 253–261
- 73 El Hanache L, Lebeau B, Nouali H, et al. Performance of surfactant-modified *BEA-type zeolite nanosponges for the removal of nitrate in contaminated water: Effect of the external surface. *J Hazard Mater*, 2019, 364: 206–217
- 74 Chutia P, Kato S, Kojima T, et al. Adsorption of As(V) on surfactant-modified natural zeolites. *J Hazard Mater*, 2009, 162: 204–211
- 75 Muir B, Bajda T. Organically modified zeolites in petroleum compounds spill cleanup—Production, efficiency, utilization. *Fuel Process Technol*, 2016, 149: 153–162
- 76 Rehakova M, Cuvanová S, Dzivak M, et al. Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. *Curr Opin Solid State Mater Sci*, 2004, 8: 397–404
- 77 Petrovic A M, Barrett W C, Larsson-Kovach I M, et al. Downward migration of metalaxyl fungicide in creeping bentgrass sand lysimeters as affected by organic waste, peat and zeolite amendments. *Chemosphere*, 1998, 37: 249–256
- 78 Bandura L, Franus M, Józefaciuk G, et al. Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup. *Fuel*, 2015, 147: 100–107
- 79 Jiang N, Shang R, Heijman S G J, et al. High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review. *Water Res*, 2018, 144: 145–161
- 80 Cheng H, Reinhard M. Sorption of trichloroethylene in hydrophobic micropores of dealuminated Y zeolites and natural minerals. *Environ Sci Technol*, 2006, 40: 7694–7701
- 81 Palmer M, Hatley H. The role of surfactants in wastewater treatment: Impact, removal and future techniques: A critical review. *Water Res*, 2018, 147: 60–72
- 82 Pukcothanung Y, Siritanon T, Rangsiwatananon K. The efficiency of zeolite Y and surfactant-modified zeolite Y for removal of 2,4-dichlorophenoxyacetic acid and 1,1'-dimethyl-4,4'-bipyridinium ion. *Microporous Mesoporous Mater*, 2018, 258: 131–140
- 83 Hailu S L, Nair B U, Redi-Abshiro M, et al. Preparation and characterization of cationic surfactant modified zeolite adsorbent material for adsorption of organic and inorganic industrial pollutants. *J Environ Chem Eng*, 2017, 5: 3319–3329
- 84 Sun K, Shi Y, Wang X, et al. Sorption and retention of diclofenac on zeolite in the presence of cationic surfactant. *J Hazard Mater*, 2017, 323: 584–592
- 85 de Ridder D J, Verberk J Q J C, Heijman S G J, et al. Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: Mechanisms and efficacy. *Sep Purif Technol*, 2012, 89: 71–77

Summary for “沸石材料在土壤修复工程中的应用研究进展”

Progress of using zeolite materials in soil remediation engineering

Shimao Deng, Zheting Chu, Jiaxin Liang, Jing Li & Hong Chen*

State Environmental Protection Key Laboratory of Integrated Surface Water Groundwater Pollution Control, Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

* Corresponding author, E-mail: chenh3@sustech.edu.cn

Soil contamination has become a global environmental crisis due to the development of the industry. Exploring cost-effective and long-term active soil remediation materials is the key to tackle the soil contamination problem. Based on excellent absorption and cation exchange capacity (CEC), zeolite molecular sieve materials have been widely used in soil remediation. Herein, we summarize the available works in the literature on conventional zeolite materials which have been applied in soil remediation. Especially, focusing on composition and structure features of zeolite materials, we elaborate on their structure-activity relationship down to details. Besides, the microscopic interaction between zeolites and soil contaminants have elucidated. The research process of zeolite used in soil remediation has been reviewed.

As discussed in this review, for the conventional zeolite materials used for soil remediation can be classified into pure zeolite materials and zeolite-based composite materials. Pure zeolite materials can be divided into natural zeolites and synthetic zeolites. Natural zeolites are cheap but with multiple elements inside the structure and composition, which is of low purity, and small pore volumes. Ion exchange, acid/alkali washing, and heat treatment are standard methods that have been used to improve the sorption capacity of natural zeolites. Compared to natural zeolites, synthetic zeolites are with tunable compositions and frameworks with high purity. But the cost for synthetic zeolites is higher, which hinders their large-scale application. In recent years, zeolite-based composite materials have been frequently employed as a composite material mixed with other kinds of materials, including nanoscale zero-valent iron or biochar, or humic acid, etc., for soil remediation. The obtained composite materials can be nanoscale zero-valent iron/zeolite composite materials (Z-nZVI), humic acids/zeolite composite materials (HZ), and biochar/zeolite composite materials (BZ). Usually, the soil remediation effect of zeolite-based composite materials is better than pure zeolite materials due to the synergy between the components.

Targeting different types of pollutants in the soil requires the dedicated zeolite materials for the treatment, and the microscopic interaction mechanism between zeolite materials and pollutants are also various. For cationic contaminants, such as heavy metal ions, zeolite with low Si/Al ratio and large pore size are effective amendments, because the soil remediation effect directly correlated to the CEC in the used materials. As most of the zeolites have a net negative structural charge, which typically results in little or no affinity for anionic species. Therefore, pure zeolite materials are rarely used for anionic pollutants remediation. While combining zeolite with other materials, such as nZVI, both the cationic and anionic pollutants in the soil can be effectively removed. Moreover, organic pollutants can also be removed by zeolite as the organic pollutants can be physically adsorbed within the zeolite channels through Van der Waals forces or hydrogen bonding. The adsorption capacity of zeolite materials on the organic matter is heavily dependent on the zeolites' pore sizes and hydrophobic properties. Usually, zeolites with a high Si/Al ratio and large pore size can be used to immobilize organic pollutants more effectively.

We concluded this review with some perspectives. We think that elucidating the remediation mechanism down to the atomic-scale and optimizing the green chemistry synthesis process for zeolites are two urgent approaches that need to be considered seriously soon.

zeolite materials, soil remediation, cation exchange, adsorption, contaminant immobilization

doi: [10.1360/TB-2020-0678](https://doi.org/10.1360/TB-2020-0678)