有机污染物在海泡石矿物的界面吸附与降解研究进展

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摘 要: 海泡石是一种典型的纤维状富镁硅酸盐粘土矿,广泛地应用于土壤污染治理、空气净化和水体污染物吸附等领域,然而海泡石表面 Si-OH 反应活性尤其是与有机污染物的反应机制尚未有清楚的认识。本文综述了海泡石对水体环境中有机污染物的界面吸附与降解研究进展,首先介绍了海泡石对有机染料、有机农药、药物和个人护理品等有机污染物的界面吸附情况,然后探讨了海泡石在深度氧化技术中通过界面吸附或者助催化协同作用提高了有机污染物去除效率的研究进展,最后指出了海泡石在有机污染物去除领域中未来的发展方向,特别是对海泡石 Si-OH 在深度氧化技术中的应用前景进行了分析。本文试图为海泡石矿物治理有机废水方面的拓展研究与应用提供指导。

关键词: 海泡石; 有机污染物; 吸附; 降解; 硫酸根自由基; 羟基自由基

中图分类号: X176 **文献标识码**: A **文章编号**: 1672-9250(2021)06-0737-13 **doi**: 10.14050/j.cnki.1672-9250.2021.49.055

海泡石是一种典型的纤维状富镁硅酸盐粘土矿,世界的储量约为 80 亿吨,主要分布在中国、西班牙、美国等国家。中国目前已经探明的海泡石储量约为 26 亿吨,主要分布在湖南、河南、河北和江西等省份[1]。海泡石是一种纤维状的含水硅酸镁,其理想化学结构式为 $Mg_8(H_2O)_4(OH)_4[Si_{12}O_{30}]\cdot nH_2O$ ($n\leqslant 8$),单元层由连续的 Si-O 四面体片和不连续的 Mg-O 八面体片按 2∶1型排列而成,具有层状和链状结构的过渡特征,并形成孔径约为 1.06 nm×0.37 nm 的特殊孔道结构,这使其具有微孔性和高比表面积[2]。海泡石在水溶液中稳定,孔道中填充着水分子和可交换的阳离子,孔道表面分布着大量的 Si-OH,并通过与金属阳离子配位而形成稳定的八面体,其在外在能量的作用下具有较高的反应活性[3-5]。海泡石特殊的化学结构及晶体结构使其具有热稳定性好、吸附容量高、催化活性好等特点,近年来其在土壤污染治理、空气净化和水体污染物吸附等领域已被日益广泛地应用[6-7],并逐渐成为当前研究的热点问题。以“sepiolite”为关键词在 web of science 中检索到文章 3 351 篇,其中 2010~2020 年度共发表 2 073 篇(图 1),约占收录文章整数的 62%,并呈现出逐年增长的趋势。

海泡石在土壤污染治理[8]和空气净化[9],特别是水体环境中有机污染物的处理[10-12]等方面有广泛的应用。有机污染物和水体环境中固体颗粒物相结合,一般主要包括有机质结合态、黑炭结合态、碳纳米材料结合态和矿物结合态等,如芳香性有机污染物分子中存在带负电荷的大 π 键使其能够吸附在多种矿物的表面[13-15]。带有极性基团的海泡石,由于强极性基团 Si-OH 的存在,一方面氧原子中的孤电子对可以充当路易斯碱,吸附带正电荷或者含有空位缺陷官能团的有机污染物,另一方面 Si-OH 具有较高的反应活性,其可以和带有-OH、-SH 和-COOH 等有机污染物发生脱水反应,进而形成带有稳定 Si-O-C 键或者 Si-O-S 键的络合物[10, 16-17]。

近年来,部分科研工作者已经将海泡石应用于水体环境中有机污染物的吸附和降解,以“sepiolite”和“organic pollut* ”为关键词在 web of science 中检

收稿日期: 2021-01-30; **改回日期**: 2021-03-23
基金项目: 国家重点研发计划项目(科技助力经济 2020 重点专项);湖南省科技托举人才项目(2020TJ-Q12);湖南省自然科学基金杰出青年项目(2021JJ10001);湖南省教育厅项目(19B133、20A114)。
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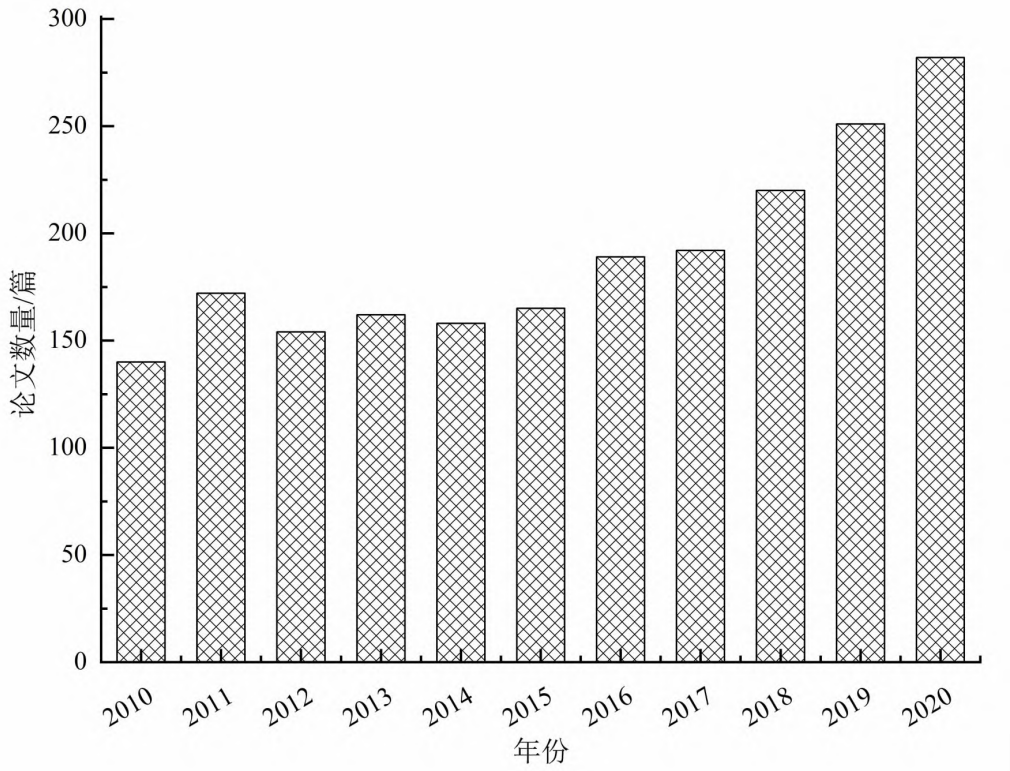

数据截止 2020 年 12 月 31 日

图 1 2010~2020 年度 web of science 收录海泡石论文数量变化图

Fig. 1 Number of published papers on sepiolite indexed by web of science from 2010 to 2020

索到相关文章 92 篇。结合中国知网的检索结果,本文对相关文献进行分析和梳理,研究了海泡石在水体环境中对有机污染物的吸附和降解两个方面的发展历程,探索海泡石在治理水体环境中有机污染物时的瓶颈问题,提出海泡石矿产资源综合利用的发展方向,从而为提升海泡石在水体环境中有机污染物治理能力和拓宽海泡石矿产资源的应用范围提供理论依据。

1 海泡石对水体环境中有机物污染物的界面吸附研究

得益于较大的比表面积和多孔道结构,海泡石在水体环境中有机污染物的治理最早主要体现在对有机污染物的吸附方面[13-15]。另一方面,海泡石结构中存在着吸附水、分子筛水、结合水和结构水四种不同形式的 Si-OH[18-19](如图 2 所示),强极性的 Si-OH 则可以通过分子之间的作用力进一步对有机污染物进行吸附[20-22]。本文将水体环境中有机污染物分为有机染料、有机农药、药物和个人护理品(PPCPs)以及其他等四类有机污染物进行概述(见表 1),阐述了海泡石通过吸附的方式对水体环境中有机污染物去除的研究进展。

1.1 海泡石对水体环境中有机染料的吸附研究

海泡石等粘土矿对有机染料废水具有较好的吸附脱色效果。自 1985 年美国建成日处理 22 700 吨废水的沸石粘土水处理装置以来,科研工作者对有机染料在海泡石上吸附行为进行了日益广泛的研究。张晴等[23]报道了海泡石原矿经过简单的酸化处理后,溶液的 pH 值是影响有机染料在海泡石表面吸附效果的最主要因素。贾堤等[24]研究发现不同价态的有机阳离子染料在海泡石表面的吸附效果有较大的差异。Omer 等[25]则研究发现甲基蓝在海泡石表界面的吸附是一个吸热过程,结晶紫的吸附则是一个放热且自发的过程。Su 等[26]采取酸活化和热处理的方式对海泡石进行预处理后对 100 mg/L 活性艳蓝进行吸附,反应 5.2 h 后其去除率达到 98.9%。Yu 等[27]报道了 MgAl 和水滑石联合对海泡石的改性,研究发现联合改性对海泡石吸附不同的阴阳离子均有显著的促进作用。Yu 等[28]发现 Pickering 泡沫改性后的海泡石对甲基橙和甲基绿的吸附量分别为 1 421.18 和 638.81 mg/g。Mahdavinia 等[29]报道在海泡石存在下,将丙烯酰胺接枝

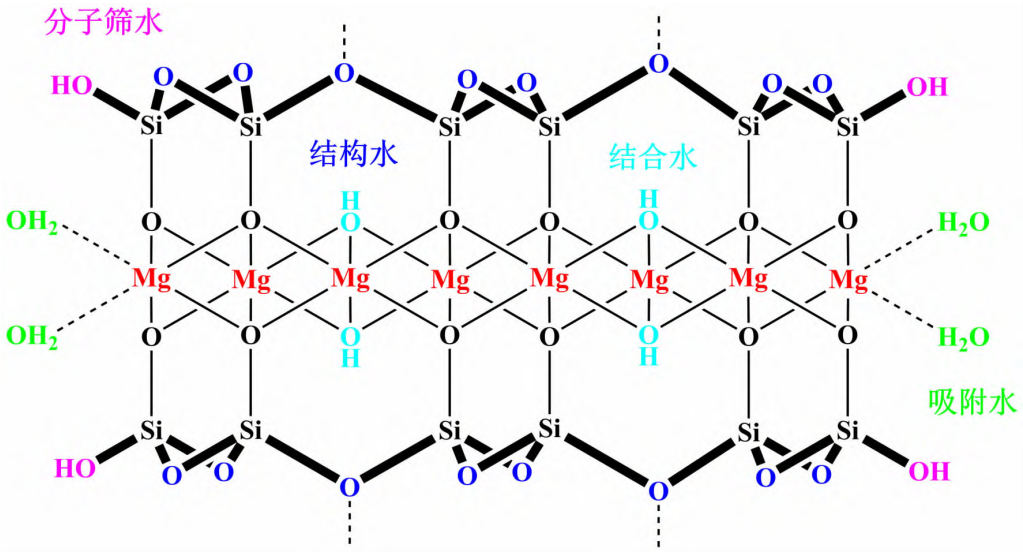

图 2　海泡石内部结构示意图

Fig. 2　Internal structure of sepiolite

到 kappa-卡拉胶生物聚合物上,并制备了纳米复合水凝胶,该纳米复合材料对结晶紫的吸附表现为准二级吸附动力学。

1.2　海泡石对水体环境中有机农药的吸附研究

海泡石对水体环境中有机农药也体现出较好的吸附去除效果。Casal 等[30]研究发现硫黄素-T 改性后的海泡石有利于氟乐灵的吸附,而阳离子表面活性剂改性则极大增强了海泡石对非极性农药甲草胺和异丙草胺的吸附效果。Salvador 等[31]研究发现林丹在 NaOH 改性后的海泡石表面具有较好的吸附作用,在微波的作用下林丹能够分解生成五氯环己烯和三氯苯等中间产物, Ni_xO_y 负载在海泡石表面时则可以直接将林丹氧化降解为 CO_2。Andrades 等[32]报道了十六烷基吡啶阳离子改性后的海泡石等对两种杀菌剂喷康唑和甲霜灵具有较好的吸附效果。关莉等[33]报道经过 300 ℃高温活化的海泡石对 40 μg/mL 吡虫啉的吸附效果达到 18.18%。Maqueda 等[34]报道在超声的辅助下,草克净的去除效果较好。科研工作者也研究了咪鲜胺[35]、苯噻酰草胺[36]、二苯并噻吩、4,6-二甲基二苯并噻吩[37]的吸附效果,部分农药的吸附去除率最高可以达到 80%以上。Sanchez-Martin 等[38]发现阳离子表面活性剂溴化十四烷基三甲胺改性后的海泡石对喷康唑、利尿隆、甲草胺、阿特拉津和甲霜灵等均具有较好的吸附效果,且不易发生脱附。Ramirez-Gomez 等[39]和 Qin 等[40]分别考察了利用 4-乙烯基吡啶/丙烯、酰胺和生物炭对海泡石进行改性后对阿特拉津农药的去除效果,发现 4-乙烯基吡啶/丙烯改性后的海泡石对阿特拉津的吸附效果最好,且 4-乙烯基吡啶的比例越高则吸附效果越好。

1.3　海泡石对水体环境中 PPCPs 的吸附研究

PPCPs 是水体环境中的一类新兴有机污染物。近年来,海泡石也被广泛地运用于水体环境中 PPCPs 的去除。如 Cuevas 等[41]报道四环素在海泡石的作用下,能达到 100% 的去除效果。Bakhtiary 等[42]报道了十六烷基吡啶鎓改性后的海泡石反应 60 min 后对 240 mmol/kg 的 2,4-二氯苯氧乙酸钠去除率达到 100%。Ezzatahmadi 等[43]利用 Fe 和 Ni 双金属共同修饰海泡石后对 2,4-二氯苯酚的去除率可达 100%。Wu 等[44]发现溴代十六烷基三甲胺(CTAB)改性后的海泡石对双酚 A 和土霉素的吸附去除率均可达 100%, SDBS 改性后的海泡石对 2.172 mg/L 土霉素吸附去除率可达到 99%。Undabeytia 等[45]发现有机硅改性大大增强了海泡石对阿替洛尔、雷尼替丁、卡马西平的吸附效果。

1.4　海泡石对水体环境中其它有机污染物的吸附研究

海泡石对石油废水、酒厂废水等同样具有较好的吸附效果。如 Sanchez-Martin 等[46]研究发现不同粘土矿物对表面活性剂的吸附顺序为十八烷基三甲基铵(ODTMA)>表面活性剂 TX-100(TX100)>>十二烷基磺酸钠(SDS),蒙脱石和伊利石对 TX100 和 ODTMA 的吸附量较高,高岭石和海泡石对 SDS 的吸附量较高。酒厂废水特点是有机物含量高,季

表 1 海泡石对水体环境中有机污染物吸附研究的文献报道

Table 1 Literature reports on adsorption of organic pollutants by sepiolite in water environment

	有机污染物	吸附剂	去除率/%	参考文献
有机染料	碱性紫 5BN 直接大红 4B 士林灰 分散棕 活性红 KD-G	SEP		[23]
	亚甲基蓝 结晶紫 甲基绿	SEP		[24]
	甲基蓝 结晶紫	SEP		[25]
	直接快速黑色	酸热/SEP	98.9	[26]
	阴阳离子染料	MgAl-LDH/SEP	99.8	[27]
	甲基绿	Pickering 泡沫/SEP	100	[28]
	结晶紫	MBA/SEP/$(NH_4)_2S_2O_8$		[29]
有机农药	氟乐灵 甲草胺或异丙甲草胺	TFT/SEP AS/SEP		[30]
	林丹	Ni_xO_y/NaOH/SEP		[31]
	喷康唑 甲霜灵	HDPY/SEP		[32]
	吡虫林	热/SEP	18.18	[33]
	草克净	超声/SEP		[34]
	咪鲜胺	SEP		[35]
	苯噻酰草胺	SEP		[36]
	二苯并噻吩 4,6-二甲基二苯并噻吩	SEP	80 56	[37]
	喷康唑、利尿隆、甲草胺、阿特拉津、甲霜灵	ODTMA/SEP		[38]
	阿特拉津	MSDS /丙烯酰胺/SEP		[39]
	阿特拉津	生物炭/SEP		[40]
PPCPs	四环素	SEP	100	[41]
	2,4-二氯苯氧乙酸钠	NCP/SEP	100	[42]
	2,4-二氯苯酚	Fe/Ni/SEP	100	[43]
	土霉素	CTAB/SEP	99.42	[44]
	土霉素	SDBS/SEP	99.01	[45]
	阿替洛尔	有机硅/SEP		
其它	表面活性剂	SDS/SEP ODTMA/SEP Triton X-100/SEP	92	[46]
	酒厂废水	结晶紫/SEP	100	[47]
	多环芳烃	SEP	100	[48]
	石油	聚氨酯海绵/SEP	100	[49]
	硝酸盐	有机改性 SEP		[50]

注: SEP=海泡石,LDH=水滑石,CTAB=十六烷基三甲基溴化铵,SDS=十二烷基硫酸钠,MBA=亚甲基双丙烯酰胺,ODTMA=溴化十四烷基三甲胺,HDPY=十六烷基吡啶阳离子,MSDS=4-乙烯基吡啶,TFT=硫黄素-T,AS=阳离子表面活性,NCP=十六烷基吡啶鎓,SDBS=十二烷基苯磺酸钠。

节性流量变化大,并且胶体分散体的失稳能够导致大量分散物质的絮凝。然而 Rytwo 等[47]研究发现用结晶紫等光敏化剂修饰后的海泡石对酒厂废水处理获得了较好的效果,1 kg 有机海泡石和 1 kg 海泡石原矿可有效去除 8 000 L 污水中的胶体颗粒。Gonzalez-Santamaria 等[48]通过将吸附等温线拟合到 Freundlich 和线性模型中,得出海泡石比史蒂芬石的吸附能力要稍弱。Qiu 等[49]采用一步法将改性的超疏水海泡石加载到三维多孔聚氨酯海绵骨架表面,所制备的超疏水海绵材料能够快速、选择性地吸收海绵重量 29 倍以上的多种油和非极性溶剂。此外,制备的复合材料可重复用于油水分离 10 次以

上,分离效率达 99.45%以上。Barroso-Solares 等[50]以有机改性海泡石为填料,采用原位聚合法制备了纳米复合亲水柔性聚氨酯泡沫塑料,该材料提高了硝酸盐对海泡石的亲和力,使硝酸盐的最大吸附量达到 23.30 mg/g。

2　海泡石对有机污染物的降解研究

深度氧化技术主要分为基于·SO_4^-[51-53]和基于·OH[54-56]的深度氧化技术,近年来海泡石在深度氧化技术中也有广泛的应用。海泡石在深度氧化技术中的应用一方面可以发挥其较大的比表面积,加大对水体环境中有机污染物的吸附;另一方面,海泡石可以发挥其助催化剂的作用,在深度氧化反应中起到电子传递作用,从而加速反应体系中活性氧物种生成效率,提高有机污染物的降解效果。

2.1　海泡石在基于·SO_4^-的深度氧化技术中对有机污染物的降解研究

目前海泡石在基于·SO_4^-的深度氧化技术体系中运用的报道不多,科研工作者主要是通过将金属氧化物负载在海泡石上,从而达到提高金属氧化物活化过硫酸盐效率的目的。例如 Wang 等[57]通过氮掺 TiO_2(N-TiO_2)和酸活化海泡石(ASEP)组成纳米复合材料(N-TiO_2/ASEP)活化过氧化单硫酸盐(PMS),研究发现 N-TiO_2/ASEP/PMS 体系在 60 min 内降解了约 95%的甲基橙,反应速率常数比 TiO_2/PMS 高出近 5.44 倍。Xu 等[58]以海泡石为载体,采用共沉淀法制备了一种新型磁性 Fe_3O_4 海泡石复合材料并活化过硫酸盐,该反应体系中 10 mmol/L 的阿特拉津的去除率达到 71.6%、TOC 去除率达到 20.9%。Zong 等[59]采用共沉淀法在改性海泡石粘土表面负载 Fe_3O_4,分别催化 $K_2S_2O_8$ 和 H_2O_2 生成·SO_4^-和·OH;反应 90 min 后,$K_2S_2O_8$ 和 H_2O_2 体系对阿特拉津的去除率分别为 65.7%和 57.8%。

2.2　海泡石在基于·OH 的深度氧化技术中对有机污染物的降解研究

基于·OH 的深度氧化技术是当前水体环境中去除有机污染物最主要的研究方式[60-61]。然而在能耗、催化剂回收、有机污染物的去除效率等方面仍然有很多需要进一步研究和提升的空间[62-63]。近年来,科研工作者将海泡石等粘土矿物应用在基于·OH 的深度氧化技术中,试图达到提高有机污染物去除效率的目的。本文将从光催化技术、(类)光芬顿技术和臭氧氧化技术等几个方面,对有机污染物的降解情况进行阐述(表 2)。

2.2.1　海泡石在光催化技术中对有机物的降解研究

光催化技术作为一种典型的基于·OH 的深度氧化技术,海泡石在其中也有广泛的应用。海泡石的加入能通过协同作用和界面效应等显著提高催化剂的光催化效果,如 Ugurlu 等[64]研究了 TiO_2/SEP 纳米颗粒光催化降解橄榄油废水中的色素、木质素和苯酚,取得了良好的降解效果。而 Du 等[65]研究发现 Ag_2O-TiO_2/SEP 在可见光(λ>420 nm)下,比 Ag_2O-TiO_2、TiO_2/SEP 和 Ag_2O/SEP 具有更高的光催化活性。这些复合材料之所以具有优异的光催化效率,是因为它们的异质结与粘土层的多孔结构之间存在协同作用,从而产生了高效的吸附和电荷分离能力。Akkari 等[66-67]考察了新型多孔 ZnO/SiO_2 海泡石异质结构作为光催化剂在降解有机染料和药物的效率,发现改性后的粘土纳米基质对布洛芬有较好的光催化降解效果。Akkari 等[68]合成的 ZnO/Fe_3O_4/SEP 在室温下表现出超顺磁性,在紫外光照射 2 h 后,亚甲基蓝完全脱色,并且在连续几个处理周期中重复使用该材料,其光催化活性仍然保持。值得注意的是,ZnO/Fe_3O_4/SEP 材料表现出与 ZnO/SEP 材料相似的活性,但具有更容易回收的优势。Jin 等[69]设计并制备了层状双氢氧化物(LDH)酸化海泡石,并同时光催化降解甲基橙和亚甲基蓝,该复合材料在可见光照射下表现出最高的光催化活性。酸处理后的海泡石比表面积大、结晶度高、表面活性位点丰富且分布均匀,从而有效提高了海泡石吸附和助催化作用。Liu 等[70]同样通过简单、低成本的溶剂热反应制备了具有吸附和降解液态有机污染物功能的介晶 TiO_2/SEP 复合材料,进一步验证了高结晶度、大的比表面积、丰富的羟基自由基和有效的光生电荷分离的协同效应有效地提高了光催化降解效果。Chuaicham 等[71]研究发现 SEP/碳纳米管复合材料比纯海泡石和碳纳米管具有更高的活性,这是由于在海泡石与碳纳米管的界面接触中产生了新的电子陷阱态,从而抑制了碳纳米管的电子复合,共同促进了环丙沙星的可见光光催化降解效果。Ezzatahmadi 等[43]研究发现海泡石作为载体材料,分散了 Fe/Ni 纳米粒子,显著降低了其聚集性,相应地提高了 2,4-DCP 的吸附和降解

表 2 海泡石在基于·OH 的深度氧化技术中对有机污染物降解的文献报道

Table 2 Literature reports on degradation of organic pollutants by sepiolite during advance oxidation technologies based on hydroxyl radicals

技术	有机污染物	反应体系	去除率/%	参考文献
光催化技术	橄榄油废水	TiO_2/SEP/SL	99	[64]
	酸性红 G	Ag_2O-TiO_2/SEP/VL		[65]
	布洛芬	ZnO/SEP/UV		[66]
	甲基蓝	ZnO/Fe_3O_4/SEP/UV	100	[67]
	甲基橙 布洛芬	ZnO/SiO_2/SEP/UV		[68]
	有机染料	LDH/SEP/VL	100	[69]
	甲基橙 甲基蓝	TiO_2/SEP/UV	91 98	[70]
	罗丹明 B	g-C_3N_4/Pd/SEP/VL		[71]
	曙红染料	TiO_2/SEP/UV	72	[72]
	四环素 甲基蓝	$BiVO_4$/SEP/VL	100	[73]
(类) 光芬顿技术	酸性橙Ⅱ	Fe (Ⅲ) /SEP/H_2O_2		[74]
	直接橙 26	Fe (Ⅲ) /SEP/H_2O_2	98	[75]
	溴氨酸	Fe/Mn/SEP/H_2O_2		[76]
	活性黑 5	Fe^0/SEP/H_2O_2/电	80~100	[77]
	罗丹明 B 4-硝基苯酚	Fe(OH) $_X$/SEP/ H_2O_2/VL		[78]
	橄榄油废水	Fe^0/SEP/ H_2O_2	60	[79]
	BDE-209	Fe^0/SEP/ H_2O_2		[80]
	罗丹明 6G	Fe^0/SEP/H_2O_2/MW	100	[81]
	布拉唑蓝 ED	Fe (Ⅲ) /SEP/ H_2O_2	96	[82]
	美托洛尔	Fe^0/SEP/ H_2O_2	67	[83]
	双酚 A	Ag/AgCl/Fe/SEP		[84]
	氧氟沙星	二茂铁/SEP/VL/ H_2O_2	100	[85]
	苯磺酸盐 偶氮复红 甲基对硫磷 结晶紫	$NiFe_2O_4$/SEP/MW/ H_2O_2	100	[86]
	双酚 A	FexOy/SEP/ H_2O_2	87	[87]
	有机碳	Fe/Mn/SEP/ H_2O_2		[88]
	甲基蓝	FeS_2/ SEP/电/ H_2O_2	100	[89]
	氧氟沙星	FeC_6@ SEP/VL/ H_2O_2		[90]
	氧氟沙星	Fe-Cu@ SEP/ H_2O_2	93	[91]
臭氧氧化技术	橄榄油废水	Fe^0/SEP/O_3		[92]
	苯酚 木质素 橄榄油废水	UV/$NaBO_3$/SEP/O_3	63 85 88	[93]
	活性橙 122	La^{3+}/WO_3/TiO_2/SEP/O_3	100	[94]
	甲基蓝	Mn/SEP/O_3	98	[95]
	喹啉	$CuFe_2O_4$/SEP/O_3	90	[96]

注: VL=可见光,UV=紫外光,SL=太阳光,MW=微波。

反应活性。De Oliveira 等[72]成功地制备了海泡石固定化 TiO_2,其对曙红染料有 72%的光催化效率。Naing 等[73]发现制备的 $BiVO_4$/SEP 纳米复合材料具有良好的可见光光催化性能,并证实了 $BiVO_4$ 与海泡石粘土之间存在较强的界面效应。光致发光和瞬态光电流响应表明,界面效应有效地促进了光生电子空穴对的分离,进一步提高了光催化性能。

2.2.2 *海泡石在(类)光芬顿技术中对有机物的降解研究*

海泡石作为载体在(类)光芬顿技术中应用广泛,如 Rodriguez 等[74]采用海泡石负载铁非均相芬顿法降解纺织废水中的染料酸性橙 II,发现该催化剂对实际的纺织废水有较好的处理效果。Asci 等[75]采用 Fe(Ⅲ)/SEP 为催化剂,在 H_2O_2 存在下对直接橙 26 进行间歇脱色研究,而 Fei 等[76]则报道了海泡石负载 Fe/Mn 多相类芬顿催化剂对溴酸水溶液的处理研究。上述两种海泡石复合材料在光芬顿技术中对污染物均体现了较好的降解效果。Iglesias 等[77]报道了 Fe^0/SEP 催化剂在光芬顿氧化体系对活性黑 5 的降解率可以达到 80%以上。Gao 等[78]探索了 $Fe(OH)_X$/SEP 在光芬顿氧化体系中对罗丹明 B 和 4-硝基苯酚同样具有较好的降解效果。Martins 等[79]报道了海泡石类芬顿法处理橄榄研磨废水,其 COD 去除率为 54%,TOC 去除率为 60%。Fu 等[80]以海泡石为载体合成纳米零价铁(nZVI),研究发现十溴二苯醚的反应速率是传统制备 nZVI 的 5 倍。Rao 等[81]同样将 nZVI 负载于高岭石和海泡石上,并应用于微波辐射下降解罗丹明 6G,同样取得了较好的降解效果。Akay 等[82]研究了实验参数对布拉唑蓝在 Fe(Ⅲ)/SEP 非均相芬顿型氧化反应体系中降解的影响,其 COD 去除率取得了较好的效果。Su 等[26]以铁锰海泡石为非均相芬顿类催化剂,研究了水溶液中活性艳蓝的脱色,该催化剂对活性艳蓝的降解具有良好的稳定性。Daneshkhah 等[83]采用海泡石负载纳米零价铁(SPT-nZVI)去除水中的美托洛尔,其降解符合假二级动力学模型。Liu 等[84]采用离子交换法和光还原法合成了一种新型的 Ag/AgCl/Fe-等离子体光芬顿催化剂,在可见光照射下该催化剂表现出很高的光催化活性。Tian 等[85]研究发现二茂铁在海泡石上具有高分散性的-C_2H_4-化学键,该催化剂在可见光(>420 nm)和过氧化氢(2.0 mmol/L)下对氧氟沙星的降解达到 100%。Shen 等[86]采用微波-水热法制备了尖晶石-$NiFe_2O_4$/天然矿物(海泡石、硅藻土和高岭土)复合材料,该材料在几分钟内可完全去除废水中的十二烷基苯磺酸钠、偶氮品红、甲基对硫磷和结晶紫等有机污染物。Xu 等[87]采用化学共沉淀法制备了磁性海泡石复合材料,在 1 000 mg/L H_2O_2 作用下,反应 30 min 后双酚 A 完全降解。Duc 等[88]将类芬顿反应与厌氧氨氧化相结合,构建了去除氮和有机碳的新工艺,该工艺对氮和 COD 的去除效果较好。Fayazi 等[89]采用海泡石/黄铁矿(SEP/FeS_2)纳米复合材料对亚甲基蓝染料进行非均相电芬顿处理,亚甲基蓝在 75 min 反应时间内几乎完全矿化。Tian 等[90]研究了二茂铁化学改性海泡石在非均相芬顿反应中提高铁效率的有效策略,并用于氧氟沙星的可见光降解,60 min 后氧氟沙星中 98.7%的 F 和 97.0%的 N 转化为 F^-和 NO_3^-,TOC 去除率为 89.35%。Tian 等[91]则以 Fe-Cu 双金属负载海泡石为催化剂,芬顿反应 60 min 后氧氟沙星的去除率为 93%。

2.2.3 *海泡石在臭氧氧化技术中对有机物的降解*

臭氧氧化技术中,海泡石一方面可以发挥吸附作用,另一方面同样也可以负载活化臭氧的催化剂。Martins 等[92]开展了 Fe/SEP/O_3 体系对橄榄木加工废水进行强化臭氧氧化的实验研究,该体系对 COD 去除率可达 80%。Ugurlu 等[93]探讨了 O_3/UV/$NaBO_3$ 及预处理对橄榄油生产废水中苯酚和木质素的脱色和去除的可行性。苯酚和木质素的降解遵循假一级动力学模型,该研究证明了光解去除有机污染物的有效性。Dincer 等[94]采用溶胶-凝胶法制备了 La^{3+}/WO_3/TiO_2/SEP 复合材料。研究了溶液初始 pH 值、催化剂用量、染料浓度、臭氧流量等参数对染料降解的影响,反应 4 h 内该染料的色度和 COD 去除率分别为 99.9%和 90%。Cheng 等[95]制备了锰沉积海泡石催化剂,该催化剂在臭氧氧化体系中对再生造纸废水不但体现了较好的处理效果还表现出良好的稳定性。Liu 等[96]采用柠檬酸盐溶胶-凝胶法制备了 $CuFe_2O_4$/SEP 纳米复合材料,该材料对喹啉体现出了较好的降解效果。

3　海泡石在水体环境中有机污染物去除应用研究展望

海泡石 Si-OH 具有不同的 Si-O 键键能[97-98],外界提供不同的能量能够导致不类型的 Si-OH 活化并进一步发生脱水反应。有趣的是,部分科研工作者研究同样证实了 Si-OH 在太阳光、可见光和紫外光等外在光源的作用下具备一定的光催化活性[99-100]。如西班牙科学家 Sastre 等[101]发现纯的硅分子筛,特别是内部结构中含有大量 Si-OH 的 β-分子筛会具有非常高的反应活性和选择性,在紫外光的辐射下发生 Si-O 断裂产生·OH,并能够将甲醇氧化成甲酸或者甲醛等物质。法国科研工作者 El-Roz

等[102]则通过把部分 Si-OH 转变为 Si-O-Ti，并着重探讨了 Si-O-Ti 和 Si-OH 的比重对光催化活性的影响，发现 Si-OH 的存在是影响 β-分子筛/TiO_2 复合材料光催化性能的主要因素。Qu 等[103]发现硅胶中的中 Si-OH 在可见光作用下能够发生 Si-O 断裂，从而形成具有高反应活性的·OH。在该体系产生的·OH 和溶解氧反应能够进一步的引发产生一系列的活性氧物种，反应产物中多个多溴联苯醚羟基化产物的存在证实了·OH 等活性物种是引起其降解的主要原因。部分科研工作者也进一步证实了 β-分子筛/TiO_2 复合材料中 Si-OH 对有机污染物降解可行性及其可能的转化机制[97, 104]。因此，探索海泡石矿物中不同种类 Si-OH 的活化方式是当前科研工作者面临的一个重要课题，Si-OH 生成活性氧物种效率的提升一方面可以为开发水环境中有机污染物处理的新材料提供理论依据，另一方面也对加快推进海泡石矿物资源整合和开发利用工作提供实验支撑。

4 结论

海泡石是一种有广泛应用前景的粘土矿物材料，其不仅通过直接界面吸附的形式对有机污染物进行吸附去除，而且还可以以助催化剂的形式对有机污染物进行降解去除。海泡石通过直接界面吸附方式，对有机染料、有机农药、药物和个人护理品以及其他有机污染物等都体现较好的去除效果，特别是针对部分低浓度的药物和个人护理品等可以达到完全去除目的。经过酸活化、碱活化、有机改性、铁磁改性或者泡沫修饰后的海泡石明显增强了对有机污染物的吸附效果。海泡石对有机污染物的降解则主要是通过在深度氧化技术中发挥助催化剂的作用。基于硫酸根自由基的深度氧化技术中，海泡石通过负载金属氧化物等活化过硫酸盐，从而产生硫酸自由基对有机污染物起到吸附和降解的协同作用。基于羟基自由基的深度氧化技术中，海泡石在光催化技术、(类) 光芬顿技术和臭氧氧化技术中均有广泛的应用。海泡石的引入，通过吸附或者助催化作用显著提高了传统深度氧化技术对有机污染物的去除效率。然而，目前关于有机污染物在海泡石表面吸附机理和降解机理的研究并不多，且不成系统，而相关机理的认识对于其后续的推广应用具有非常重要的意义。因此，为了深入开展海泡石在水体环境中有机污染物的去除研究及拓展应用，下一步应着重从以下三个方面入手：(1) 阐明不同种类的有机污染物在海泡石界面的吸附机制；(2) 开发海泡石 Si-OH 活化方法并直接作用于水体环境中有机污染物的降解，探明海泡石对有机污染物的降解机制；(3) 加大海泡石复合材料的开发力度，提高复合材料吸附和催化的协同能力。

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Research Progress on Adsorption and Degradation of Organic Pollutants on Sepiolite Mineral Interface

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Abstract: Sepiolite is a typical fibrous magnesium rich silicate clay ore, which is widely used in soil pollution control, air purification and water pollutant adsorption. However, the Si-OH reactivity of sepiolite surface, especially the reaction mechanism with organic pollutants, has not been clearly recognized. In this paper, the research progress of interface adsorption and degradation of organic pollutants in water environment by sepiolite is reviewed. The interface adsorption of organic pollutants such as organic dyes, organic pesticides, drugs and personal care products by sepiolite was introduced, and the research progress of sepiolite in advanced oxidation technologies to improve the removal efficiency of organic pollutants by interfacial adsorption or co-catalysis was discussed, the future development direction of sepiolite in the field of organic pollutant removal was pointed out, especially the application prospect of sepiolite Si-OH in advanced oxidation technologies was analyzed. This paper attempts to provide guidance for the research and application of sepiolite in the treatment of organic wastewater.

Key words: sepiolite; organic pollutants; adsorption; degradation; sulfate radical; hydroxyl radical