



矿物材料去除水中抗生素的研究进展

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[摘要] 近年来, 水中新兴污染物引发的环境问题越来越受到人们的重视。抗生素属于新兴污染物之一, 其难降解、用量大且无法被完全吸收利用。残留的抗生素排放到水环境中逐渐积累, 给生态环境造成不良影响。矿物材料具有成本低、处理工艺简单等优点, 被广泛用于去除水中的抗生素。对抗生素在环境中的危害进行介绍, 描述了抗生素进入不同水环境的方式, 同时对黏土、金属矿物及其他矿物材料去除水中抗生素的方法进行总结, 并对不同材料的去除能力进行比较。黏土矿物的吸附作用、Fenton 反应以及光催化反应均能有效去除水中的抗生素。在实际应用中, 应根据抗生素的含量选择合适的处理方法, 并注意不同工艺之间的相互配合。

[关键词] 抗生素; 矿物材料; 新兴污染物; 水处理

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Research progress of antibiotic removal from water using mineral materials

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Abstract: In recent years, environmental problems caused by emerging pollutants in water have attracted increasing attention. As one of the emerging contaminants, antibiotics are difficult to degrade, in large amounts, and cannot be fully absorbed and utilized. Residual antibiotics are discharged into the environment and gradually accumulate, causing adverse effects on the ecological environment. Mineral materials are widely used to remove antibiotics from water because of their low cost and simple treatment process. The hazards of antibiotics in the environment, and the ways in which antibiotics enter different water environments were described. The removal of antibiotics from water by clay, metallic minerals and other mineral materials were summarized and the removal capacities of different materials were compared. It was found that the adsorption of clay minerals, Fenton reaction and photocatalytic reaction could effectively remove antibiotics from water. In practical application, appropriate methods should be selected according to the content of antibiotics, and attention should be paid to the cooperation between different processes.

Key words: antibiotics; mineral material; emerging contaminants; water treatment

近年来, 科学工作者发现一些新兴污染物(EC)如治疗药物、化妆品和香料等进入环境后会破坏生态过程, 对人类和生态环境造成不良影响^[1]。常用的抗生素药物如阿莫西林、青霉素和红霉素等多用于治疗细菌和其他微生物引起的炎症。由于抗生素大多数为水溶性, 不易被肠道吸收^[2], 代谢不完全, 部分抗生素以母体形式伴随其代谢产物排出体外, 从而进入环境中。这些化合物在水中持久性强、难降解, 经市政污水处理厂(STP)处理后仍有残留^[3],

加速致病菌抗药性的形成。抗生素在水环境中的积累引起人们对其潜在毒性和生态影响的关注。快速有效降解环境中的抗生素成为近年来科学研究的重要课题。

去除抗生素常见的方法有吸附法、生物电化学法、膜生物反应器(MBR)、电化学法、人工湿地和高级氧化法(AOPs)等。此外, 碳纳米材料^[4]、g-C₃N₄^[5]、藻类^[6]、微生物^[7]等也用于抗生素的去除中。与人工合成材料相比, 矿物材料具有储藏量大、生产成本

低、操作方便等特点,在不同抗生素处理工艺均有广泛应用^[8]。笔者对抗生素在水中积累的方式,矿物材料去除抗生素的应用情况进行了总结和分析,以期为研究人员了解抗生素的积累,选择合适的去除方法提供一定理论依据。

1 抗生素进入水环境的途径

抗生素根据化学结构可分为氟喹诺酮类、四环素类、 β -内酰胺类、大环内酯类、磺酰胺类等,目前其用量处于较高水平且持续增加,导致水中的抗生素不断积累。抗生素进入不同水生环境的途径如图1所示。

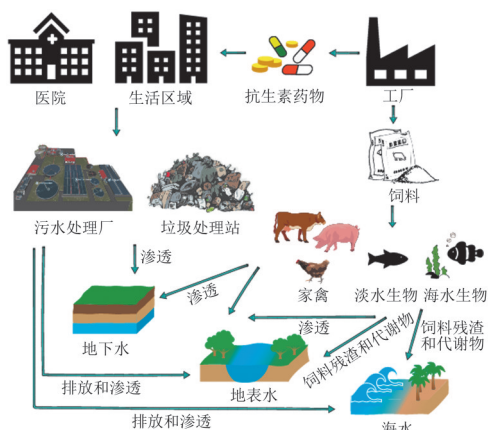
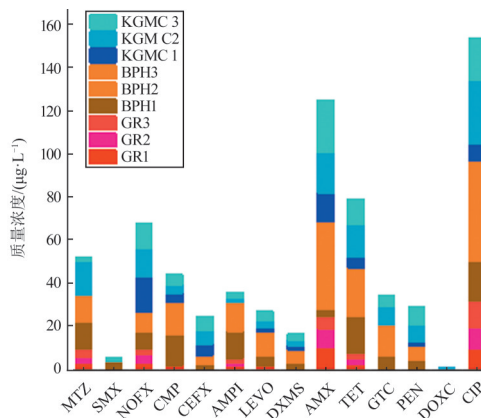


图1 抗生素进入不同水生环境的途径

Fig. 1 Pathways of antibiotics entering different aquatic environments

仅有25%的抗生素会被人体或动物体有效吸收利用^[9],其余部分随代谢产物被排出体外,通过下水道进入城市水循环系统,随后流入污水处理厂。污水处理厂通过凝结、沉淀、消毒和澄清处理以去除废水中的部分污染物,但其工艺并非专注于抗生素类污染物,处理后的废水仍包含多种抗生素^[10],被排放到地表水中。医院废水、制药厂排放污水、农牧场动物的排便中含有的抗生素不会被环境降解,也会在地表水中不断积累,被认为是抗生素进入地表水的重要来源。调查显示^[11],临近农场的河流更易检出抗生素,其次为医院和制药厂。以美国某地区为例^[12](图2),多种抗生素在地表水中的浓度都达到 $\mu\text{g/L}$ 级,环丙沙星(CIP)、阿莫西林(AMX)、四环素(TET)和诺氟沙星(NOFX)等常用抗生素的积累达到较高水平。除用量外,积累量还与抗生素的环境稳定性有关。四环素和氟喹诺酮类抗生素的疏水

性好,且与黏土或有机颗粒具有相互作用,更易被悬浮物吸收,因此这几种抗生素更易在水中积累。水环境中抗生素的积累会扰乱水生生态系统,加速抗药性的产生。



GR—Gomti河; BPH—医院; KGMC—乔治国王医学院

图2 美国某地区水中抗生素统计数据

Fig. 2 Statistics of antibiotics in water in some area of the United States

海水中的抗生素多数源于水产养殖。鱼类饲料中的抗生素可作为生长促进剂,未被食用的饲料及鱼类代谢后残留的抗生素残留在海水和养殖厂沉积物中^[13]。抗生素在海水中不断富集,超过生态系统的自净能力^[14],导致海产品中也开始含有抗生素。相比于地表水中抗生素的进入方式,抗生素进入海水的方式较少但更直接,且没有相关机构进行处理。控制海水中抗生素的增加应尽量从源头出发,控制甚至杜绝含抗生素类饲料的使用。

STP完成处理工作后会产生生物固体残渣,通常可作为肥料施用到土地中^[10]。若此地区土壤具有高渗透性,地下水位相对较浅,施用肥料中含有的大量抗生素无法被作物完全吸收,剩余抗生素则会进入地下水^[15]。城市下水道系统的老化和恶化,使部分污水泄漏或渗入周围的土壤中,随后污水中的抗生素和其他污染物将进入浅层地下水^[16]。在池塘进行水产养殖时,水中残留和沉积物中含有的抗生素会不断渗透到地下水中^[17]。此外,养殖场粪堆的长期堆积也是抗生素渗透进入地下水的途径之一^[18]。

2 矿物材料去除抗生素

2.1 黏土及其改性材料

黏土是土壤的重要成分,由岩石风化、侵蚀、沉积而成^[19],具有纤维状、片层状和空心管状3种结构

(见图3)^[20-23],其储量丰富,在工业、陶瓷和环境处理方面都有重要应用。黏土对抗生素药物具有高亲和力,在制药工业中可用作药物载体,增强药物的稳定性,也可用作胃肠道保护剂。黏土通过离子交换、氢键和范德华力将抗生素容纳到层间间隔中,可去除水中残留的抗生素^[24],是一种良好的吸附剂材料。但仅用黏土去除抗生素的能力有限,需进一步改性。改性方法有催化剂负载^[25]、有机改性^[20]、离子改性^[26]和磁改性^[27]等。A. M. AWAD等^[21]研究了天然和改性黏土材料对有机污染物的吸附情况,指出黏土成本较碳材料的低,且对一些有机物的吸附能力比碳材料高,在去除环境污染物方面有广泛应用。

不同类型黏土的特点、改性方法及去除抗生素的能力如表1所示。

蒙脱石是一种片层状的黏土,具有结晶度高、阳离子交换容量(CEC)高、比表面积较大的特点^[46],有大量研究将其用于抗生素的吸附。蒙脱石在低酸性溶液中对环丙沙星的吸附容量高达330 mg/g^[29],若处于碱性环境中吸附量有所下降。蒙脱石的吸附能

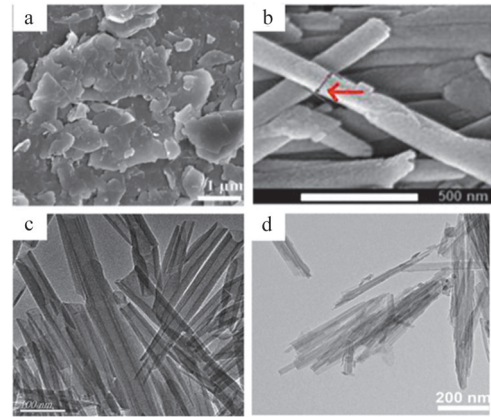


图3 蛭石(a)、埃洛石(b)的SEM照片及埃洛石(c)、坡缕石(d)的TEM照片

Fig. 3 SEM of vermiculite(a), halloite(b), and TEM of halloite(c), palygorskite(d)

力也受温度和抗生素浓度的影响,温度和抗生素浓度越高,其吸附能力越弱。为达到更高的吸附效果,可在蒙脱石表面涂覆TiO₂或ZnO纳米颗粒^[47],或引入Fe³⁺和Mn⁴⁺^[48],改性后的材料能完全去除水中的土霉素。将磁性材料负载到蒙脱石能提高其吸附能

表1 黏土矿物对抗生素的吸附性能

Table 1 Adsorption properties of clay minerals for antibiotics

项目	改性剂或方法	可吸附的抗生素	最大吸附容量/(mg·g ⁻¹)	文献
蒙脱石	Na ⁺ 改性	土霉素(OTC)	213.6	[28]
	Ca ²⁺ 改性	环丙沙星(CIP)	330.0	[29]
	阳离子表面活性剂	阿莫西林(AMX)	339.4	[30]
	阳离子表面活性剂	磺胺甲噁唑(SMX)	246.4	[30]
	聚氧乙烯20油醚	甲氧苄啶(TRI)	119.9	[30]
	Ca ²⁺ 改性	萘啶酸(NA)	24.0	[19]
	双十二烷基二甲基溴化铵	青霉素G(PEN-G)	23.0	[31]
蛭石	十二烷基二甲基甜菜碱	盐酸四环素(TC)	39.8	[20]
	磷脂酰胆碱	OTC	24.0	[32]
	磷脂酰胆碱	CIP	23.5	[32]
	表面活性剂	SMX	63.1	[33]
伊利石	—	TC	32.0	[34]
	—	CIP	33.0	[35]
埃洛石	—	OTC	52.4	[36]
	—	CIP	21.7	[37]
海泡石	—	马波沙星(MAR)	132.0	[38]
	—	恩诺沙星(ENR)	112.0	[38]
	十六烷基三甲基溴化铵、十二烷基苯磺酸钠	OTC	41.3	[39]
	—	TC	250.0	[40]
	—	氯四环素(CTC)	329.8	[41]
坡缕石	—	OTC	207.5	[41]
	十六烷基三甲基溴化铵	TC	114.6	[42]
	十六烷基三甲基溴化铵	CTC	198.2	[42]
	硅酸锌杂化	TC	337.0	[43]
	硅酸锌杂化	金霉素(AMC)	384.0	[43]
	Fe ³⁺ 改性	OTC	69.9	[44]
	酸改性	AMX	65.6	[45]
	酸改性	氨苄青霉素(AMP)	57.1	[45]

力,吸附质的分离也更加方便^[49]。

伊利石结构与蒙脱石类似,但其层间阳离子为钾离子,电荷小且不易被交换,吸附抗生素的能力不如蒙脱石,常用于吸附一些金属离子。M. MEZNI等^[50]将伊利石制成人工合成沸石,提高了天然伊利石的吸附能力,可从水溶液中有效吸收去除恩诺沙星。改性伊利石对抗生素能达到较高的吸附水平。

蛭石具有大的表面积、良好的吸附能力,可净化水中的污染物。蛭石与有机分子复合后具有疏水性^[51],对抗生素的吸附能力大幅提高。蛭石经两性表面活性剂改性后能同时改善对水中抗生素及重金属离子的亲和力^[20],可更好地去除污染物。

坡缕石和海泡石的主要结构形态为纤维状,比表面积大、孔隙多、成本低、储量大,可用于修复水中的重金属和有机物等。经硅酸盐杂化后的坡缕石对四环素类抗生素的吸附容量最高可达 329.84 mg/g^[41],与蒙脱土一样属于较高水平。坡缕石吸附多种抗生素时,先吸附疏水性较强的抗生素,使其有机碳含量增加,疏水性变强,之后吸附疏水性较弱的抗生素时受初始 pH 的影响变小^[52]。海泡石和坡缕石虽然都具有较高的吸附能力,但单独探讨其吸附抗生素的研究较少。大多数研究者考虑其优异的吸附能力和较大的比表面积,且吸附仅发生在矿物外表面,不影响对抗生素的进一步处理^[38],将这 2 种物质用作复合材料的载体,以得到活性更高的催化剂或氧化剂。如将光催化剂 $g-C_3N_4$ 负载到海泡石后^[53],黏土表面带负电的电子可减少电子和空穴的复合,有效提高了催化剂降解环丙沙星的能力。H. H. NAING 等^[54]将钨酸铋($BiVO_4$)负载到海泡石,发现光催化降解四环素的能力提高了 2 倍。

埃洛石是黏土中少有的具有空心管状结构的吸附剂,可用作纳米容器、纳米载体及吸附材料,去除水和空气中的污染物^[55]。以埃洛石为模板、KOH 为活化剂、无毒且可再生的羧甲基纤维素钠(CMC)为碳前体,可制得分级多孔碳^[56]。该碳材料具有较强的吸附能力,对氯霉素的吸附量可达 769.95 mg/g。Yue MA 等^[57]用埃洛石开发出多孔分子印迹聚合物(PMIP),具有良好的稳定性和再生能力,可选择性吸附抗生素。D. PAPOULIS^[58]总结了埃洛石复合方法及其去除各污染物的应用,发现复合埃洛石材料光催化降解抗生素的能力变强,在去除四环素方面

有极大应用前景。朱鹏飞等^[59]将光催化剂 Ag_3PO_4 负载于埃洛石,两者产生了界面效应和量子化效应,可更好、更稳定地降解水中残留的抗生素。

对于具有片状结构的黏土特别是蒙脱石,其层间可交换的阳离子较多,促进了与无机、有机阳离子的相互作用^[60],吸附容量高于其他类型的黏土。吸附能力差的黏土可通过离子改性^[35]增加可供交换的离子,扩大层间间隙,从而达到较高的吸附水平。在过酸或过碱的环境中,离子交换作用会减弱,仅依靠氢键或范德华力等分子间的相互作用,吸附作用大大减弱^[29],因此研究黏土的最适 pH 是提升吸附能力的必备环节。经有机改性^[47]和表面活性剂改性^[22]后,黏土表面与抗生素结合的位点变多,吸附能力也有较大提升。酸改性^[51]则利用黏土的溶胀性扩大结构的间隙,达到增强吸附能力的目的。负载光催化剂后,除吸附作用外,黏土材料又具有降解性能,去除能力更强。综上,黏土矿物与抗生素有很好的亲和力,是一种良好的吸附剂,通过增加接触位点、扩大结构间间隙或负载其他催化剂(见图 4)^[36, 47-54],可成为有效的抗生素去除材料。

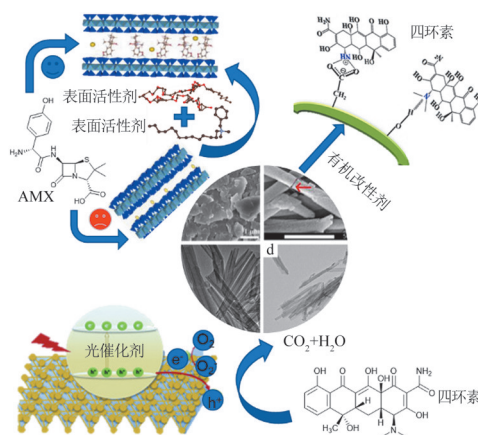


图4 黏土改性方法及其去除抗生素机理

Fig. 4 Clay modification method and its mechanism for removing antibiotics

2.2 金属矿物及其改性材料

黏土矿物等非金属材料对抗生素的处理大多属于物理吸附过程。金属矿物对抗生素类化合物同样有亲和力,并伴有络合反应发生^[61],但对抗生素的吸附能力较低,远低于黏土类^[62]。金属矿物较多应用于高级氧化工艺(AOP)去除水环境中的抗生素,通过 Fenton 反应、臭氧氧化和光催化等过程产生具

有强氧化性的活性氧(ROS)和羟基自由基($\cdot\text{OH}$),有效降解水中的有机污染物。

经典Fenton反应用铁离子和 H_2O_2 产生 $\cdot\text{OH}$ 来降解污染物,因反应必须处于酸性环境,有大量铁离子残留,限制了其处理污染物的应用。Xiaocheng LIU等^[63]介绍了Fenton反应的改进方法及反应机理(见图5),指出用Fenton反应去除抗生素时应考虑副产物的生成及降低成本。可用于Fenton反应的天然铁矿石有黄铁矿、黄铜矿和针铁矿等。某些矿物中含有 Cu^{2+} 或在水中可自发形成 H_2O_2 和 $\cdot\text{OH}$,与Fenton法可产生协同作用,即类Fenton反应(F-1)。黄铜矿在反应中可产生 Fe^{2+} 和 H^+ ,减少催化剂用量,同时促进pH的调节^[64]。C. DROGUETT等^[65]用黄铜矿作为非均相催化剂添加到异质电催化Fenton反应中,进行紫外(UV)照射,开发出新型非均相光电Fenton(HPEF)模式,并证明该模式可有效提高Fenton反应矿化头孢氨苄的能力。同样地,黄铁矿^[66]也可通过HPEF模式降解水中的抗生素。针铁矿广泛存在于自然界中^[67],但仅具有非均相催化降解抗生素的能力,不能进行光催化降解过程。在含羧基生物炭的存在下^[26],针铁矿可与其发生协同作用,对抗生素的降解能力变强。金属矿物在抗生素去除工艺中的应用情况如表2所示。

光催化反应是常见的高级氧化工艺之一。半导体被光源照射后产生活性电子-空穴对,与环境中的氧和水结合后生成超氧自由基($\text{O}_2^{\cdot-}$)和 $\cdot\text{OH}$,可加速氧化、还原反应和自由基反应。A. FUJISHIMA等^[78]发现 TiO_2 可用于光催化反应后,研究者不断寻

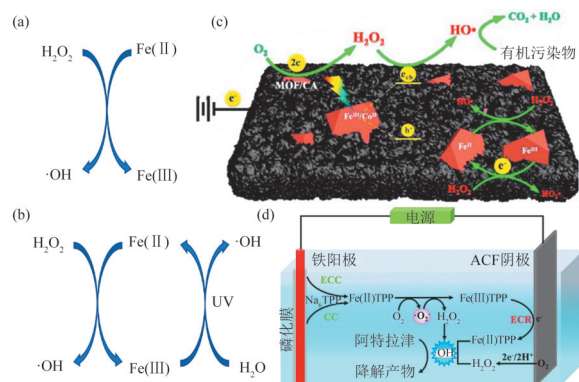


图5 Fenton反应(a)、光化学Fenton(b)、光电化学Fenton(c)、电化学Fenton(d)的反应机理

Fig. 5 Mechanism of Fenton (a), PF (b), PEF (c) and EF (d)

求改性方法或新的光催化剂材料,对金属氧化物及改性方法的研究成为热点。金红石、锐钛矿和钛铁矿等^[75]主要成分为金属氧化物,仅需简单操作即可用于光催化反应,成本低且具有较好的光催化性能。部分研究中的光催化剂仅响应紫外光,实际应用时可考虑用于紫外光照射消毒环节,增强对紫外光的利用率。构建非均相催化机制也可用于抗生素的降解,针铁矿经等离子体处理后表面的羟基密度升高^[74],可有效降解磺胺吡啶。不使用其他处理工艺,仅靠水中存在的 Cu^{2+} 、 Fe^{2+} 和 Zn^{2+} 等金属离子也可促进抗生素的氧化或水解^[79]。斑铜矿是一种Fe-Cu双金属硫化物矿物^[77],在弱酸环境中会释放 Fe^{2+} 和 Cu^{2+} ,在短时间内可活化过硫酸盐(PS),能够去除水中81.6%的四环素。

2.3 其他材料

油页岩主要由无定形硅石、石英及各种辅助矿

表2 金属矿物对抗生素的去除性能

Table 2 Removal performance of minerals for antibiotics

项目	处理工艺	抗生素	质量浓度/($\text{mg}\cdot\text{L}^{-1}$)	矿化能力/%	文献
黄铜矿	EF	TC	89.0	98.0	[64]
	HPEF	CEFX	50.0	92.0	[65]
黄铁矿	EF	SMT	55.7	95.0	[68]
	EF	LEVO	83.6	95.0	[69]
	HPEF	TAP	50.0	85.0	[66]
	F-1	TC	50.0	85.0	[70]
	催化氧化	TC	50.0	46.1	[71]
针铁矿	F-1	SMX	20.0	27.0	[72]
	F-1	NOFX	10.0	27.4	[73]
	F-1	OFX	20.0	44.8	[26]
	催化臭氧化	SSZ	10.0	56.7	[74]
钛铁矿	光催化	SFZ	10.0	35.0	[75]
	CWPO-光辅助	SFZ	10.0	85.0	[75]
锐钛矿	光催化	TC	10.0	29.6	[76]
斑铜矿	催化氧化	TC	150.0	48.7	[77]

物组成,对有机物和无机物都有很强的亲和性,可用于吸附水中的污染物。在高温条件下,油页岩吸附抗生素的性能比其他材料好得多^[80]。浮石具有较大的表面积,常被用作水处理中的吸附剂和载体材料,弱酸条件和 Cu^{2+} 能提高浮石的吸附能力,可高效去除四环素^[81]。电气石是一种环状硅酸盐矿物,包含多种金属离子^[82],可用于修复被污染的土壤。Wenzhen DUAN等^[37]用电气石吸附环丙沙星,但其吸附效果不如埃洛石和黑云母,需进一步优化。硅藻土是一种硅质岩石,成本低、储量大,可开发作为废水处理的吸附剂。将硅藻土浸泡在氯化铜溶液中即可完成改性^[83],操作简单,改性后的材料可高效吸附四环素。

生物炭和黏土矿物都是较廉价易获得的材料,且都可用于吸附水中的抗生素,若将这两种材料复合^[84],材料的表面活性和表面积均得到提升,吸附抗生素的能力变强。腐殖酸可用于改良土壤结构,对金属离子或有机污染物有吸附作用,也可通过复合方法进行改良^[85]。Yuan LI等^[86]开发了腐殖酸/膨润土复合材料,可固定水中的 Zn^{2+} ,从而抑制抗生素抗性基因的传播,对去除环境中的抗生素药物也起到一定作用。不足之处在于加入可溶性腐殖酸后,矿物材料达到吸附平衡的时间变长^[87],且对反应条件有较高要求。

3 总结与展望

抗生素的滥用及难降解性质导致水环境中的抗生素不断积累,生态环境平衡遭到破坏,耐药菌数量增多。减少环境中存在的抗生素已成为亟待解决的科学问题。通过控制抗生素滥用及加强废水处理能力可减少环境中的抗生素。黏土对抗生素有很好的吸附作用,且可达到食用级别,制作抗生素类药物或饲料时可添加部分黏土作载体,未被利用的抗生素会固定在黏土上,从而减少抗生素进入水环境中。

目前对水中抗生素的处理研究较多采用Fenton反应、光催化和吸附技术。其中矿物材料吸附去除抗生素时受环境影响较大,在不同pH下去除能力差别很大,研制出的新材料首先应探讨最适pH,处理时使用对应的缓冲溶液以保持高效的去除能力。黏土仅需简单吸附即可去除大量抗生素,达到饱和状态后通过调节pH将吸附物排出,方便再回收利用,且成本低、工艺简单,适于农场、医院和制药厂等含

抗生素较多且复杂的环境使用。Fenton反应和光催化反应工艺复杂,可用于污水处理厂的最后处理环节,去除含量较低的污染物,确保进入自然环境中的水不再含有抗生素。

目前大多数研究集中在实验室阶段,污水处理的大规模应用较少涉及,且缺少动力学数据。考虑到自然环境中存在不同种类的抗生素或其他有机污染物,单一处理技术或材料往往无法完全去除废水中所有污染物,因此将不同处理工艺集成到现有废水处理系统中意义重大。

参考文献

- [1] BOLONG N, ISMAIL A F, SALIM M R, et al. A review of the effects of emerging contaminants in wastewater and options for their removal[J]. Desalination, 2009, 239(1/2/3): 229-246.
- [2] LIU Hong, MA Chuanxin, CHEN Guangcai, et al. Titanium dioxide nanoparticles alleviate tetracycline toxicity to *Arabidopsis thaliana* (L.) [J]. ACS Sustainable Chemistry & Engineering, 2017, 5(4): 3204-3213.
- [3] NIKOLAOU A, MERIC S, FATTA D. Occurrence patterns of pharmaceuticals in water and wastewater environments [J]. Analytical and Bioanalytical Chemistry, 2007, 387(4): 1225-1234.
- [4] MINALE M, GU Zaoli, GUADIE A, et al. Application of graphene-based materials for removal of tetracyclines using adsorption and photocatalytic-degradation: A review [J]. Journal of Environmental Management, 2020, 276: 111310.
- [5] NIU Jinfen, WANG Kai, MA Z, et al. Application of g-C₃N₄ matrix composites photocatalytic performance from degradation of antibiotics [J]. Chemistry Select, 2020, 5(40): 12353-12364.
- [6] WEI Lianxue, LI Haixiao, LU Jinfeng. Algae-induced photodegradation of antibiotics: A review [J]. Environmental Pollution, 2021, 272: 115589.
- [7] SHAO Sicheng, WU Xiangwei. Microbial degradation of tetracycline in the aquatic environment: A review [J]. Critical Reviews in Biotechnology, 2020, 40(7): 1010-1018.
- [8] 刘云,董元华,杭小帅,等. 环境矿物材料在土壤环境修复中的应用研究进展[J]. 土壤学报, 2011, 48(3): 629-638.
LIU Yun, DONG Yuanhua, HANG Xiaoshuai, et al. Advances in application of environmental mineral materials in soil environment remediation [J]. Acta Pedologica Sinica, 2011, 48(3): 629-638.
- [9] ZHANG Yan, LI Aolin, DAI Tianjiao, et al. Cell-free DNA: A neglected source for antibiotic resistance genes spreading from WWTPs [J]. Environmental Science & Technology, 2018, 52(1): 248-257.
- [10] PRUDEN A. Balancing water sustainability and public health goals in the face of growing concerns about antibiotic resistance [J]. Environmental Science & Technology, 2014, 48(1): 5-14.
- [11] CHEN Yongshan, XI Xiuping, XU Jinghua, et al. Distribution pat-

- terns of antibiotic residues in an urban river catchment[J]. *Water and Environment Journal*, 2019, 33(1): 31–39.
- [12] JHA R R, SINGH N, KUMARI R, et al. Ultrasound-assisted emulsification microextraction based on a solidified floating organic droplet for the rapid determination of 19 antibiotics as environmental pollutants in hospital drainage and Gomti River water[J]. *Journal of Separation Science*, 2017, 40(13): 2694–2702.
- [13] HAN Ying, WANG Jing, ZHAO Zelong, et al. Fishmeal application induces antibiotic resistance gene propagation in mariculture sediment [J]. *Environmental Science & Technology*, 2017, 51(18): 10850–10860.
- [14] LIU Sisi, ZHAO Hongxia, LEHMLER H J, et al. Antibiotic pollution in marine food webs in Laizhou Bay, North China: Trophodynamics and human exposure implication [J]. *Environmental Science & Technology*, 2017, 51(4): 2392–2400.
- [15] LI Xunde, ATWILL E R, ANTAKI E, et al. Fecal indicator and pathogenic bacteria and their antibiotic resistance in alluvial groundwater of an irrigated agricultural region with dairies [J]. *Journal of Environmental Quality*, 2015, 44(5): 1435–1447.
- [16] ROEHRDANZ P R, FERAUD M, LEE D G, et al. Spatial models of sewer pipe leakage predict the occurrence of wastewater indicators in shallow urban groundwater [J]. *Environmental Science & Technology*, 2017, 51(3): 1213–1223.
- [17] AVISAR D, LEVIN G, GOZLAN I. The processes affecting oxytetracycline contamination of groundwater in a phreatic aquifer underlying industrial fish ponds in Israel [J]. *Environmental Earth Sciences*, 2009, 59(4): 939–945.
- [18] LI Xiaohua, LIU Chong, CHEN Yongxing, et al. Antibiotic residues in liquid manure from swine feedlot and their effects on nearby groundwater in regions of North China [J]. *Environmental Science and Pollution Research International*, 2018, 25(12): 11565–11575.
- [19] WU Qingfeng, LI Zhaohui, HONG Hanlie. Adsorption of the quinolone antibiotic nalidixic acid onto montmorillonite and kaolinite [J]. *Applied Clay Science*, 2013, 74: 66–73.
- [20] YANG Shanshan, HUANG Zhiyan, LI Chunquan, et al. Individual and simultaneous adsorption of tetracycline and cadmium by dodecyl dimethyl betaine modified vermiculite [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, 602: 125171.
- [21] AWAD A M, SHAIKH S M R, JALAB R, et al. Adsorption of organic pollutants by natural and modified clays: A comprehensive review [J]. *Separation and Purification Technology*, 2019, 228: 115719.
- [22] LIU Guangfei, ZHANG Yuanyuan, YU Huali, et al. Acceleration of goethite-catalyzed Fenton-like oxidation of ofloxacin by biochar [J]. *Journal of Hazardous Materials*, 2020, 397: 122783.
- [23] CHENG Wei, KALAHROODI E L, MARSAC R, et al. Adsorption of quinolone antibiotics to goethite under seawater conditions: Application of a surface complexation model [J]. *Environmental Science & Technology*, 2019, 53(3): 1130–1138.
- [24] DA ROCHA M C, DE ARAUJO BRAZ E M, HONÓRIO L M C, et al. Understanding the effect of UV light in systems containing clay minerals and tetracycline [J]. *Applied Clay Science*, 2019, 183: 105311.
- [25] 樊杰明, 王继全. g-C₃N₄/粘土复合光催化材料降解污染物的研究进展 [J]. *建材世界*, 2019, 40(3): 1–5.
FAN Jieming, WANG Jiquan. Research progress on g-C₃N₄/clay composite photocatalytic materials for degradation of pollutants [J]. *The World of Building Materials*, 2019, 40(3): 1–5.
- [26] ZHAO Yanping, GU Xueyuan, GAO Shixiang, et al. Adsorption of tetracycline (TC) onto montmorillonite: Cations and humic acid effects [J]. *Geoderma*, 2012, 183/184: 12–18.
- [27] TOKARČIKOVÁ M, BARDOŇOVÁ L, SEIDLEROVÁ J, et al. Magnetically modified montmorillonite – characterisation, sorption properties and stability [J]. *Materials Today: Proceedings*, 2021, 37: 48–52.
- [28] ARISTILDE L, LANSON B, CHARLET L. Interstratification patterns from the pH-dependent intercalation of a tetracycline antibiotic within montmorillonite layers [J]. *Langmuir*, 2013, 29(14): 4492–4501.
- [29] WANG C J, LI Zhaohui, JIANG W T, et al. Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite [J]. *Journal of Hazardous Materials*, 2010, 183(1/2/3): 309–314.
- [30] DE OLIVEIRA T, FERNANDEZ E, FOUGÈRE L, et al. Competitive association of antibiotics with a clay mineral and organoclay derivatives as a control of their lifetimes in the environment [J]. *ACS Omega*, 2018, 3(11): 15332–15342.
- [31] SAITOH T, SHIBAYAMA T. Removal and degradation of β -lactam antibiotics in water using didodecyl dimethyl ammonium bromide-modified montmorillonite organoclay [J]. *Journal of Hazardous Materials*, 2016, 317: 677–685.
- [32] LIU Shuai, WU Pingxiao, YU Langfeng, et al. Preparation and characterization of organo-vermiculite based on phosphatidylcholine and adsorption of two typical antibiotics [J]. *Applied Clay Science*, 2017, 137: 160–167.
- [33] WANG Jie, GAO Manglai, DING Fan, et al. Organo-vermiculites modified by heating and gemini pyridinium surfactants: Preparation, characterization and sulfamethoxazole adsorption [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2018, 546: 143–152.
- [34] CHANG P H, LI Zhaohui, JEAN J S, et al. Adsorption of tetracycline on 2:1 layered non-swelling clay mineral illite [J]. *Applied Clay Science*, 2012, 67/68: 158–163.
- [35] WANG C J, LI Zhaohui, JIANG W T. Adsorption of ciprofloxacin on 2:1 dioctahedral clay minerals [J]. *Applied Clay Science*, 2011, 53(4): 723–728.
- [36] RAMANAYAKA S, SARKAR B, COORAY A T, et al. Halloysite

- nanoclay supported adsorptive removal of oxytetracycline antibiotic from aqueous media [J]. *Journal of Hazardous Materials*, 2020, 384: 121301.
- [37] DUAN Wenzhen, WANG Ningfen, XIAO Weilong, et al. Ciprofloxacin adsorption onto different micro-structured tourmaline, halloysite and biotite [J]. *Journal of Molecular Liquids*, 2018, 269: 874-881.
- [38] STURINI M, SPELTINI A, MARASCHI F, et al. Removal of fluoroquinolone contaminants from environmental waters on sepiolite and its photo-induced regeneration [J]. *Chemosphere*, 2016, 150: 686-693.
- [39] WU Jiayan, WANG Yanhua, WU Zixuan, et al. Adsorption properties and mechanism of sepiolite modified by anionic and cationic surfactants on oxytetracycline from aqueous solutions [J]. *Science of the Total Environment*, 2020, 708: 134409.
- [40] CUEVAS J, DIROCIE N, YUNTA F, et al. Evaluation of the sorption potential of mineral materials using tetracycline as a model pollutant [J]. *Minerals*, 2019, 9(7): 453.
- [41] TIAN Guangyan, WANG Wenbo, ZONG Li, et al. A functionalized hybrid silicate adsorbent derived from naturally abundant low-grade palygorskite clay for highly efficient removal of hazardous antibiotics [J]. *Chemical Engineering Journal*, 2016, 293: 376-385.
- [42] 秦小宁. 改性凹凸棒土和膨润土对水中四环素类抗生素的吸附去除研究[D]. 兰州: 兰州交通大学, 2020.
- QIN Xiaoning. Adsorption removal of tetracycline antibiotics from aqueous solution by modified attapulgite and bentonite [D]. Lanzhou: Lanzhou Jiaotong University, 2020.
- [43] WANG Wenbo, TIAN Guangyan, ZONG Li, et al. Mesoporous hybrid Zn-silicate derived from red palygorskite clay as a high-efficient adsorbent for antibiotics [J]. *Microporous and Mesoporous Materials*, 2016, 234: 317-325.
- [44] 陈静. 改性凹凸棒土的制备及其对土霉素的吸附研究[D]. 西安: 西安建筑科技大学, 2019.
- CHEN Jing. Preparation of modified attapulgite and analysis on adsorption of oxytetracycline [D]. Xi'an: Xi'an University of Architecture and Technology, 2019.
- [45] 王姗姗, 张宇峰, 罗平, 等. 改性凹凸棒土对水中抗生素的吸附作用[J]. *净水技术*, 2017, 36(1): 42-48.
- WANG Shanshan, ZHANG Yufeng, LUO Ping, et al. Adsorption of antibiotics in aqueous solution with modified attapulgite [J]. *Water Purification Technology*, 2017, 36(1): 42-48.
- [46] BIZI M, EL BACHRA F E. Evaluation of the ciprofloxacin adsorption capacity of common industrial minerals and application to tap water treatment [J]. *Powder Technology*, 2020, 362: 323-333.
- [47] KHOSRAVI R, ZAREI A, HEIDARI M, et al. Application of ZnO and TiO₂ nanoparticles coated onto montmorillonite in the presence of H₂O₂ for efficient removal of cephalexin from aqueous solutions [J]. *Korean Journal of Chemical Engineering*, 2018, 35(4): 1000-1008.
- [48] KARPOV M, SEIWERT B, MORDEHAY V, et al. Transformation of oxytetracycline by redox-active Fe(III)- and Mn(IV)-containing minerals: Processes and mechanisms [J]. *Water Research*, 2018, 145: 136-145.
- [49] 张娟. 磁性蒙脱石的制备及其对四环素与环丙沙星的吸附性能研究[D]. 南京: 南京理工大学, 2019.
- ZHANG Juan. Preparation of magnetic montmorillonite and its adsorption properties for tetracycline and ciprofloxacin [D]. Nanjing: Nanjing University of Science and Technology, 2019.
- [50] MEZNI M, SAIED T, HORRI N, et al. Removal of enrofloxacin from aqueous solutions using illite and synthetic zeolite X [J]. *Surface Engineering and Applied Electrochemistry*, 2017, 53(1): 89-97.
- [51] 刘帅. 蛭石的有机改性及其对抗生素和环境激素的吸附性能研究[D]. 广州: 华南理工大学, 2017.
- LIU Shuai. The organic modification of vermiculite and its adsorption performance study on antibiotics and environmental hormones [D]. Guangzhou: South China University of Technology, 2017.
- [52] 全瑶. 氧氟沙星在凹凸棒土上的吸附特征研究[D]. 北京: 中国地质大学, 2017.
- QUAN Yao. Study on ofloxacin sorption characteristics to attapulgite [D]. Beijing: China University of Geosciences, 2017.
- [53] CHUAICHAM C, PAWAR R R, KARTHIKEYAN S, et al. Fabrication and characterization of ternary sepiolite/g-C₃N₄/Pd composites for improvement of photocatalytic degradation of ciprofloxacin under visible light irradiation [J]. *Journal of Colloid and Interface Science*, 2020, 577: 397-405.
- [54] NAING H H, WANG Kai, LI Yuan, et al. Sepiolite supported BiVO₄ nanocomposites for efficient photocatalytic degradation of organic pollutants: Insight into the interface effect towards separation of photogenerated charges [J]. *Science of the Total Environment*, 2020, 722: 137825.
- [55] ANASTOPOULOS I, MITTAL A, USMAN M, et al. A review on halloysite-based adsorbents to remove pollutants in water and wastewater [J]. *Journal of Molecular Liquids*, 2018, 269: 855-868.
- [56] ZHANG Ruilong, ZHOU Zhiping, XIE Atian, et al. Preparation of hierarchical porous carbons from sodium carboxymethyl cellulose via halloysite template strategy coupled with KOH-activation for efficient removal of chloramphenicol [J]. *Journal of the Taiwan Institute of Chemical Engineers*, 2017, 80: 424-433.
- [57] MA Yue, DAI Jiangdong, WANG Lulu, et al. Fabrication of porous molecularly imprinted polymer using halloysite nanotube as template for selective recognition and separation of chloramphenicol [J]. *Journal of the Iranian Chemical Society*, 2020, 17(3): 555-565.
- [58] PAPOULIS D. Halloysite based nanocomposites and photocatalysis: A review [J]. *Applied Clay Science*, 2019, 168: 164-174.
- [59] 朱鹏飞, 段明, 王萍萍, 等. Ag₃PO₄/埃洛石可见光催化降解抗生

- 素性能研究[J]. 非金属矿, 2020, 43(4): 92-95.
- ZHU Pengfei, DUAN Ming, WANG Pingping, et al. Visible light photocatalytic degradation of antibiotics by $\text{Ag}_3\text{PO}_4/\text{halloysite}$ [J]. Non-Metallic Mines, 2020, 43(4): 92-95.
- [60] YANG J H, LEE J H, RYU H J, et al. Drug-clay nanohybrids as sustained delivery systems [J]. Applied Clay Science, 2016, 130: 20-32.
- [61] LI Xiangzhi, BI Erping. Different surface complexation patterns of gatifloxacin at typical iron mineral/water interfaces [J]. Environmental Earth Sciences, 2019, 78(21): 630.
- [62] WU Tingwen, XUE Qiang, LIU Fei, et al. Mechanistic insight into interactions between tetracycline and two iron oxide minerals with different crystal structures [J]. Chemical Engineering Journal, 2019, 366: 577-586.
- [63] LIU Xiaocheng, ZHOU Yaoyu, ZHANG Jiachao, et al. Insight into electro-Fenton and photo-Fenton for the degradation of antibiotics: Mechanism study and research gaps [J]. Chemical Engineering Journal, 2018, 347: 379-397.
- [64] BARHOUMI N, OLVERA-VARGAS H, OTURAN N, et al. Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopyrite [J]. Applied Catalysis B: Environmental, 2017, 209: 637-647.
- [65] DROGUETT C, SALAZAR R, BRILLAS E, et al. Treatment of antibiotic cephalexin by heterogeneous electrochemical Fenton-based processes using chalcopyrite as sustainable catalyst [J]. Science of the Total Environment, 2020, 740: 140154.
- [66] THIAM A, SALAZAR R, BRILLAS E, et al. In-situ dosage of Fe^{2+} catalyst using natural pyrite for thiamphenicol mineralization by photoelectro-Fenton process [J]. Journal of Environmental Management, 2020, 270: 110835.
- [67] 蒋芬芬, 吴宏海. 针铁矿非均相 Fenton 法降解抗生素的特征及其动力学研究 [J]. 矿物学报, 2012, 32(S1): 144-145.
- JIANG Fenfen, WU Honghai. Characterization of antibiotic degradation by non-homogeneous Fenton method of needle ferrite and its kinetics [J]. Acta Mineralogica Sinica, 2012, 32(S1): 144-145.
- [68] BARHOUMI N, OTURAN N, OLVERA-VARGAS H, et al. Pyrite as a sustainable catalyst in electro-Fenton process for improving oxidation of sulfamethazine. Kinetics, mechanism and toxicity assessment [J]. Water Research, 2016, 94: 52-61.
- [69] BARHOUMI N, LABIADH L, OTURAN M A, et al. Electrochemical mineralization of the antibiotic levofloxacin by electro-Fenton-pyrite process [J]. Chemosphere, 2015, 141: 250-257.
- [70] MASHAYEKH-SALEHI A, AKBARMOJENI K, ROUDBARI A, et al. Use of mine waste for H_2O_2 -assisted heterogeneous Fenton-like degradation of tetracycline by natural pyrite nanoparticles: Catalyst characterization, degradation mechanism, operational parameters and cytotoxicity assessment [J]. Journal of Cleaner Production, 2021, 291: 125235.
- [71] RAHIMI F, VAN DER HOEK J P, ROYER S, et al. Pyrite nanoparticles derived from mine waste as efficient catalyst for the activation of persulfates for degradation of tetracycline [J]. Journal of Water Process Engineering, 2021, 40: 101808.
- [72] ZHUAN Run, WANG Jianlong. Enhanced degradation and mineralization of sulfamethoxazole by integrating gamma radiation with Fenton-like processes [J]. Radiation Physics and Chemistry, 2020, 166: 108457.
- [73] CHEN Xiaoying, ZHUAN Run, WANG Jianlong. Assessment of degradation characteristic and mineralization efficiency of norfloxacin by ionizing radiation combined with Fenton-like oxidation [J]. Journal of Hazardous Materials, 2021, 404: 124172.
- [74] PELALAK R, ALIZADEH R, GHARESHABANI E. Enhanced heterogeneous catalytic ozonation of pharmaceutical pollutants using a novel nanostructure of iron-based mineral prepared via plasma technology: A comparative study [J]. Journal of Hazardous Materials, 2020, 392: 122269.
- [75] GARCÍA-MUÑOZ P, PLIEGO G, ZAZO J A, et al. Sulfonamides photoassisted oxidation treatments catalyzed by ilmenite [J]. Chemosphere, 2017, 180: 523-530.
- [76] WU Suqing, LI Xueyan, TIAN Yanqin, et al. Excellent photocatalytic degradation of tetracycline over black anatase- TiO_2 under visible light [J]. Chemical Engineering Journal, 2021, 406: 126747.
- [77] ZHANG Xin, DENG Honghu, ZHANG Guoquan, et al. Natural bornite as an efficient and cost-effective persulfate activator for degradation of tetracycline: Performance and mechanism [J]. Chemical Engineering Journal, 2020, 381: 122717.
- [78] FUJISHIMA A, HONDA K. Electrochemical photolysis of water at a semiconductor electrode [J]. Nature, 1972, 238(5358): 37-38.
- [79] CHEN Jiabin, WANG Ying, QIAN Yajie, et al. $\text{Fe}(\text{III})$ -promoted transformation of β -lactam antibiotics: Hydrolysis vs oxidation [J]. Journal of Hazardous Materials, 2017, 335: 117-124.
- [80] GOUZA A, SAOIABI S, EL KARBANE M, et al. Oil shale powders and their interactions with ciprofloxacin, ofloxacin, and oxytetracycline antibiotics [J]. Environmental Science and Pollution Research, 2017, 24(33): 25977-25985.
- [81] GULER U A, SARIOGLU M. Removal of tetracycline from wastewater using pumice stone: Equilibrium, kinetic and thermodynamic studies [J]. Journal of Environmental Health Science & Engineering, 2014, 12: 79.
- [82] 殷丹阳, 史静, 许正文, 等. 电气石吸附喹诺酮类抗生素的吸附特性研究 [C]. 第十三届全国水处理化学大会暨海峡两岸水处理化学研讨会, 2016.
- [83] LI Guoting, FENG Yanmin, ZHU Weiyong, et al. Enhanced adsorptive performance of tetracycline antibiotics on lanthanum modified diatomite [J]. Korean Journal of Chemical Engineering, 2015, 32(10): 2109-2115.

(下转第 45 页)