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污水硫自养反硝化技术研究进展

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摘　要:硫自养反硝化(SAD)是一种绿色低碳的污水脱氮技术,具有成本低、污泥产量少、无须外加有机碳源等优点,已成为污水脱氮技术研究的热点之一。阐述SAD填料组成与复合硫源填料的合成方法,归纳SAD固定床反应器和流化床反应器的结构及其适用条件,回顾SAD与电化学、异养反硝化、厌氧氨氧化耦合工艺等方面的研究进展,并总结SAD耦合技术的优缺点以及耦合工艺的脱氮特征。微生物的代谢功能是实现高效SAD的关键因素,列举不同代谢特性的SAD功能微生物种类,阐述代表性微生物*Thiobacillus*和*Sulfurimonas*在SAD过程中的反硝化特性及其生长条件。目前,SAD技术在填料、反应器和耦合工艺等方面取得显著进步,但仍面临诸多挑战,在SAD技术温度适应性、高处理负荷反应器设计以及工艺流程优化等方面进一步创新。

关键词:反硝化;污水脱氮;污水处理;研究进展

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Research progress of sulfur autotrophic denitrification in wastewater

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Abstract: Sulfur autotrophic denitrification (SAD) has become one of the hotspots in nitrogen removal technology during wastewater treatment because of its characteristic green and low-carbon technology for nitrogen removal from sewage, which has the advantages of low cost, low sludge yield and no need for organic carbon sources. In this paper, the research progress on SAD of carrier compositions and synthesis method of composite sulfur source filler. The structure and applicable conditions of SAD packed bed reactor and fluidized bed reactor were summarized. The research progress of SAD coupled with electrochemical, heterotrophic denitrification and Anammox technology was reviewed. The advantages and disadvantages of SAD coupled

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technology were summarized. The metabolic function of microorganisms is a key factor in the realization of effective SAD. This review enumerates the types of SAD functional microorganisms with different metabolic characteristics, the denitrification characteristics and growth conditions of *Thiobacillus* and *Sulfurimonas* in the SAD process were described. Currently, SAD technology has made significant progress in the fields of filler, reactor and coupling process, but still faces many challenges, further innovations have been made in temperature adaptability of SAD technology, reactor design with high treatment load, and process optimization.

Keywords: denitrification; sewage nitrogen removal; sewage treatment; research progress

中国市政生活污水处理碳源不足问题突出,控氮减碳特别是低C/N污水中硝酸盐的低碳处理已成为行业重大技术挑战[1]。现有污水处理常常需要补充有机碳源以提升反硝化效能,在主流的异养生物反硝化处理中额外投加的有机碳源转化为大量污泥和二氧化碳,这是与污水低碳理念背道而驰的无奈之举。污水的绿色低碳处理已成为环境工程技术研究的热点,是构建可持续水循环系统的重要途径。

硫自养反硝化(SAD)是通过活性污泥中的SAD菌,硫化物作为电子供体,NO_3^-作为电子受体,将NO_3^-和NO_2^-转化为N_2进而达到脱氮的效果。其中反硝化体系中的反硝化微生物将NO_3^-还原为N_2或N_2O的过程为:$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$[2-4]。并且SAD工艺污泥产量低,无须添加有机碳源,能克服传统异养反硝化缺点,具有很广阔的应用前景。

随着“双碳”目标深入推进,具有绿色低碳特征的SAD技术愈发受到科研领域的关注。近几年来,SAD技术在工艺和反硝化微生物作用机制方面取得了新的进展。笔者简述不同种类SAD填料的研究进展,从反应器构型和工艺耦合等角度对SAD及SAD水处理集成工艺技术的研究进行回顾和总结,并展望该技术未来发展方向。

1 SAD填料

电子供体是SAD技术中反应效果及效率的决定性因素[5]。目前在SAD技术中应用较广泛的电子供体主要有S^0和S^{2-},常见对应的还原性含硫物质分别为单质硫、硫化亚铁等,它们可以分别制成不同类型的填料:单质硫与硫化物填料、复合硫源填料。

1.1 单质硫与硫化物填料

单质硫填料价格低、毒性小、便于运输和操作,在SAD技术中被广泛使用。研究表明,单质硫填料粒径越小,比表面积就越大,给微生物提供的代谢结合位点越多,可以更好地提升反硝化效率。粒径0.8、3 mm的单质硫填料在经过培养后,当进水NO_3^--N浓度为80～90 mg/L时,粒径0.8 mm填料的TN去除率达到87%,粒径3 mm硫磺填料TN去除率仅71%[6]。粒径0.5～1.0 mm的硫磺填料在用于生活污水处理时,SAD系统硝酸盐去除率可以达到84.86%[7]。

但单质硫的低水溶性(5 μg/L 20 ℃)导致脱氮效率难以进一步提升[8],因此,含硫化合物(如:Fe_2S_3、H_2S、$Na_2S_2O_3$等)成为更适宜的电子供体,当硫化铁填料用于处理地下水时,可以同时去除亚砷酸盐和硝酸盐,出水浓度分别低至(7.84±7.29) μg/L和(3.78±1.14)mg/L[9]。另外,将H_2S作为硫源,二氧化碳为无机碳源,同时使用磷矿石补充碱度,在脱氮效率达到99.1%的同时解决了SAD工艺中pH值降低的问题,优化了SAD的运行效率[10]。

1.2 复合硫源填料

SAD工艺中会消耗大量碱度,降低出水pH值[11],进而导致污泥酸化。SAD的理想辅助填料应当能补充碱度且避免增加出水硬度,因此,引入石灰石、牡蛎壳等可提供碱度的pH值调节材料制成复合硫源填料,可显著提升SAD效率。例如,将硫粉和石灰石以1:1的比例通过胶凝黏附法制备硫-石灰石复合硫源填料,将其应用于生活污水尾水的深度脱氮,对TN去除率为90%左右,而未投加填料的去除率仅在80%[12]。但硫-石灰石复合硫源填料存在一些弊端,如出水硬度高、SO_4^{2-}含量升高等问题。为此,也有学者用其他填料代替石灰石,如贝壳[13]、沸石[14]、陶粒[15]和珊瑚石[16]等。

不仅如此,最优的SAD辅助填料还应当能保障填料具有良好透气性和传质条件,并且能为微生物生长提供良好环境。因此,提高填料比表面积有利于增加SAD微生物的附着生长和提升反硝化速率,一些可强化反硝化效率的新型复合硫源填料应运而生。例如,采用包埋法制备的硫铁生物填料具有疏松多孔结构,有效提高了填料的比表面积,在进水硝酸盐浓度为30 mg/L、HRT为10 h时脱氮效率可以达到99.8%[17],相比简易复合硫源填料提高了10%左右。此外,利用混合烘干等方式制备的固体复合填料也可以提高脱氮效率,同时使得SAD系统

在微生物富集和稳定S/C比方面表现良好;例如将硫磺粉、粉末活性炭和碳酸钙混合后烘干制成3~5 mm的复合填料,相比未投加填料对TN的去除率提高了40%左右[18]。将熔融态硫单质、蛋壳或扇贝壳粉末、石灰石粉末混合制成粒状均质复合硫源填料,在处理地下水硝酸盐时,反硝化效率超过99.7%,并且能为SAD过程提供充足的碱度与无机碳源[19]。

2 SAD生物反应器

SAD填料的形式多种多样,常有不同类型的反应器与之匹配。基于填料在反应器中的状态分为填充床反应器和流化床反应器两大类。

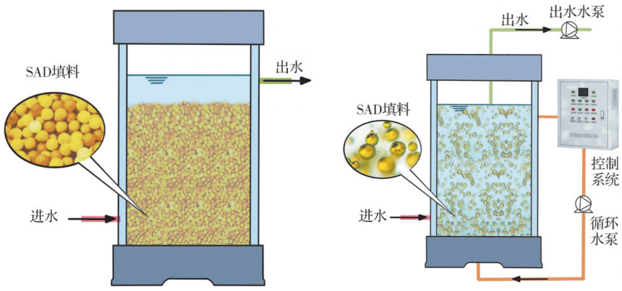
2.1 SAD填充床反应器

SAD填充床反应器(如图1(a))适用机械强度弱、密度大、不易堵塞的填料,水质适用范围广。使用单质硫-碳酸钙颗粒混合填料时,填充床反应器的脱氮效率可以达到膜生物反应器的两倍[20];但混合填料存在堵塞、污染的问题,因此,在此基础上发展出了使用复合硫源填料SAD填充床反应器,对饲料废水的处理负荷达到0.36 kg/(m³·d)[21]。此外,SAD填充床反应器被成功应用于地下水硝酸盐污染控制、城市污水深度脱氮等:当采用硫-石灰多孔陶瓷为载体的3 L填充床反应器处理污染地下水时,反应器反硝化效率达到99.5%[22];采用体积为0.8 L的玉米芯-硫为填料的填充床反应器处理城市污水时,最低出水NO_3^--N浓度为0.31 mg/L,去除率为98.62%[23]。SAD填充床反应器仍存在一些缺点,其单位体积负荷相对较低,不适合大规模污水脱氮处理工程。

2.2 SAD流化床反应器

SAD流化床反应器(如图1(b))具有传质条件好、单位体积负荷高、高速脱氮且低成本[24]等优点,但对填料要求较高,需要使用密度低且有一定机械强度的悬浮填料。在厌氧连续流流化床膜生物反应器(AnFB-MBR)中使用S^0颗粒填料和Fe^0颗粒填料,颗粒填料与水接触面积大,处理效率提升显著,AnFB-MBR的硝酸盐去除率高达98%,相比于同条件下的SAD填充床反应器的脱氮效率提高了4.4倍,并有效抑制了SO_4^{2-}的生成和pH值的降低[25]。不同电子供体在流化床反应器中拥有不同的脱氮效率,FeS_2驱动的反硝化过程仅产生少量SO_4^{2-},无须调节pH值,反硝化速率最高可达到142.2 mg/(L·d);但S^0驱动的反硝化过程需要碳酸钙保持pH值为中性,因此会产生更多的污泥(硫酸钙沉淀),反硝化速率最高为184.4 mg/(L·d)[26]。

综上,填料的内部结构和不同的电子供体对反应器的脱氮效果均有影响,此外,不同的进水污水种类、水力停留时间、反应器的传质性能、排气排泥的效率等诸多因素对脱氮的影响都值得探究。在研究中需将这些参数进行模拟和优化,以设计最佳反应器构建形式,使脱氮效率进一步提高。



(a) SAD填充床反应器　(b) SAD流化床反应器

图1　SAD反应器类型示意图

Fig. 1　Schematic diagram of SAD reactor type

3 SAD水处理集成工艺

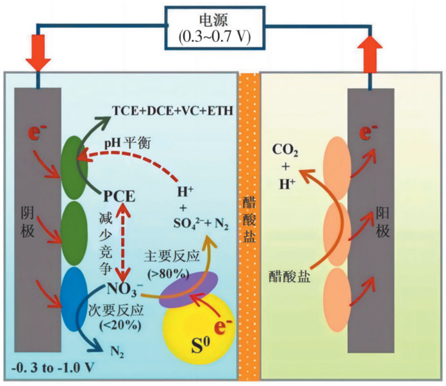
SAD过程会消耗硫源与碱度,并产生SO_4^{2-}副产物,将其与其他生物技术组合,优势互补,形成耦合工艺,能提升反硝化系统的抗冲击负荷能力,降低副产物和工艺运行成本,具有很好的应用前景。

3.1 SAD-电化学工艺

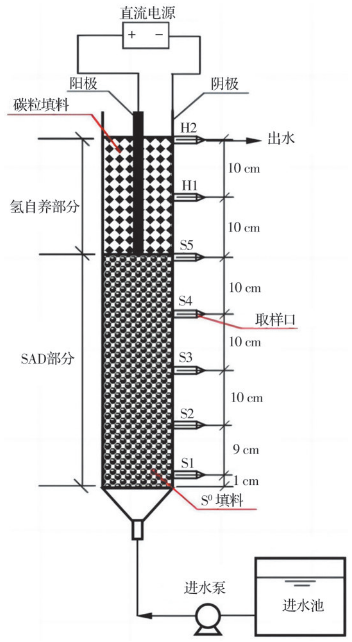
SAD耦合电化学工艺(如图2(a))的优势主要在于:1)SAD产生的H^+可被电化学反应中和,保持出水pH值的稳定。SAD(S室)-电化学氢自养(H室)耦合工艺(图2(b))可以同时去除ClO_4^-和NO_3^-,S室产生的H^+被H室中的电化学反应消耗(图2(c)),实现了出水pH值的稳定[27]。2)电化学直接产氢还原硝酸盐可以降低SAD负荷,减少副产物SO_4^{2-}的产生。在电极驱动的硫自养反硝化工艺中,SAD过程对硝酸盐去除的贡献率为75.3%~83.1%,SO_4^{2-}产量降低了17%~25%[28];此外,S^0粒子和电极都作为反硝化细菌的生物载体,促进了硫粒子和阴极上协同反硝化群落和功能基因的形成[29]。还有相当一部分的SAD-电化学工艺研究集中在反应器设计、脱氮性能与工艺优化等方面。例如:生物电化学和SAD耦合体系[30]、基于质子交换膜电渗析(PEMED)的SAD脱氮体系[31]等,均可实现90%左右的硝酸盐去除率,其中,PEMED的SAD脱氮体系无亚硝酸盐积累,且pH值稳定。

3.2 SAD-异养反硝化(HD)耦合脱氮

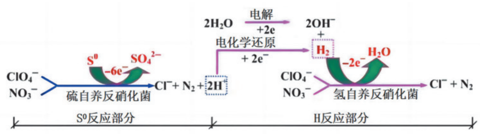
SAD和HD耦合有以下优点:1)无须外加有机碳源,降低了运行成本;2)减少副产物SO_4^{2-}的生成[33];3)脱氮效率大幅提高,污泥产量降低[34]。因此,有很多研究将SAD引入污水生化处理中,大多



(a) 硫自养-电化学耦合工艺机理示意图[32]



(b) 某种硫自养-电化学反硝化耦合装置示意图[27]

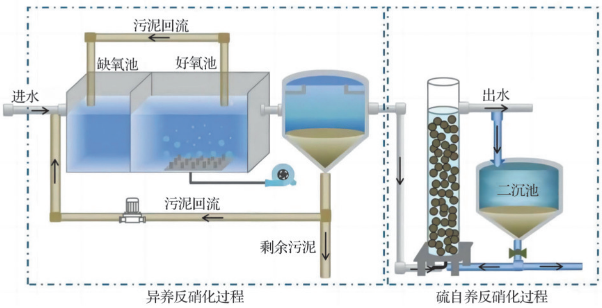


(c) 硫自养-电化学反硝化耦合装置中 NO_3^- 和 ClO_4^- 还原路径示意图[27]

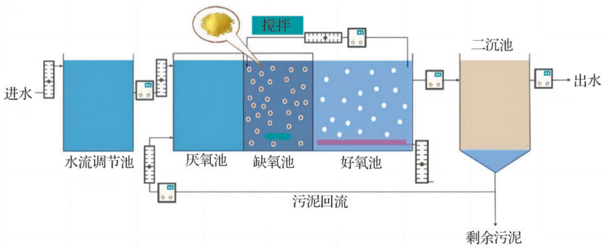
图 2　SAD-电化学耦合工艺示意图

Fig. 2　Schematic diagram of sulfur autotrophic-electrochemical coupling process

以SAD滤池为深度处理单元(图3(a))。在污水深度脱氮工艺中,SAD滤池在未外加有机碳源的情况下,脱氮效率可以与投加了外碳源的HD滤池相当,硝酸盐去除率达到了(0.268±0.047)kg/(m^3·d),大大降低了运行成本[35]。以SAD滤池的形式耦合HD有着造价高、工艺流程长的缺点,因此,直接将SAD引入HD单元实现高效耦合,促进了异养反硝化和SAD协同脱氮,NO_3^--N和TN的去除效率分别达到98.9%和95.7%[2]。近期也有研究将SAD与A^2O结合到同一反应器或工艺中,即将硫源填料(如S^0、$CaCO_3$、PAC和$NaSiO_3$混合制成的复合填料)投加进A^2O反应器中(图3(b));结果TN的去除率由50.2%提高至81.2%,SO_4^{2-}实际平均生成量为(235.39±43.37) mg/L,小于SO_4^{2-}生成量理论值[36],说明SAD和A^2O工艺耦合不仅可以提高脱氮效率,还减少了SAD过程中SO_4^{2-}的生成量,也可能有利于降低污泥产量,无须碳源实现绿色低碳脱氮。



(a) 污水处理工艺后接SAD滤池示意图[37]



(b) 投加了硫基载体的A^2O工艺示意图[36]

图 3　SAD-异养反硝化耦合工艺示意图

Fig. 3　Schematic diagram of coupling process of sulfur autotrophic-heterotrophic denitrification

3.3　SAD-厌氧氨氧化耦合工艺

厌氧氨氧化(Anammox)的优势同SAD一样,即无须外加有机物、无须曝气,可以大大节约经济成本,但Anammox过程将水中污染物NO_2^--N和NH_4^+转化为N_2的同时产生了NO_3^--N,导致出水硝酸盐含量升高[38],而SAD过程将水中NO_3^-转化为N_2的同时导致副产物NO_2^--N、H^+和SO_4^{2-}的生成。因此,将SAD与Anammox耦合可以有效取长补短。大多数研究表明,SAD耦合Anammox工艺(SDA工艺)后总氮去除率高达95%以上[39-41]。SDA工艺不仅脱氮效率高,还有以下优点:1)SAD中的硫氧化细菌(SOB)对硫化物的快速氧化可以缓解硫化物对SDA体系中Anammox的抑制作用[42];2)Anammox可以为SAD过程提供碱度,平衡SDA工艺出水pH值[43];3)Anammox可以消除SAD失衡导致过量生成的NO_2^--N,减少出水副产物[44]。

将SAD耦合部分硝化-厌氧氨氧化(PNA)工艺有着同样的作用机制,与传统的PNA和SAD工艺相比,耦合工艺中SAD产生的NO_2^--N易被PNA反应所利用,可实现SO_4^{2-}产量降低59%,总脱氮效率

达到98%[45]。因此,耦合工艺系统较SAD或Anammox更加稳定,运行操作简单、脱氮效率高。

4　硫自养反硝化微生物

微生物的代谢功能是实现高效SAD的关键。SAD的功能微生物种类、生长条件及其生理特性见表1。其中,硫氧化细菌(SOB)是一类将单质硫或低价的还原性硫化物部分氧化为高价硫化物或完全氧化为硫酸盐(SO_4^{2-})的菌群[46]。SOB菌种类多样,分布广泛,其中一部分SOB菌能够利用还原性硫化物作为电子供体来还原NO_3^-或NO_2^-[47-48],是参与SAD过程的关键微生物。

*Thiobacillus*和*Sulfurimonas*是已报道的最普遍的两种SAD细菌,在SAD过程中,它们易受到如电子受体不同、水中有机碳含量和电子供体浓度等环境因素影响,使其相对丰度发生变化。Chen等[49]研究发现,当电子受体从NO_3^-转变为NO_2^-,*Thiobacillus*显著增加,且SAD系统表现出较强的处理能力。不仅如此,水中有机碳含量也是影响细菌组成的重要因素,有机组分可抑制*Thiobacillus*生长,而*Sulfurovum*更适合在有机碳丰富的条件下生存[50];在C/N从2.7减小至0的过程中,*Sulfurovum*的相对丰度由15.4%降至0.9%,而*Thiobacillus*成为主要优势菌落,相对丰度达到0.1%~50.2%[51]。此外,*Thauera*作为SAD过程中的重要异养硝酸盐还原菌,其在低硫化物浓度的条件下可以和*Thiobacillus*共同维持体系脱氮平衡[52]。许多研究[11, 53-54]也表明,在SAD过程中,*Proteobacteria*是SAD中主要优势菌门,*Sulfurimonas denitrificans* (*e-proteobacteria*)和*Thiobacillus denitrificans* (*β-proteobacteria*)是SAD过程中最常见的优势菌属,它们普遍是嗜中性粒细胞或嗜中温的,广泛分布在海洋和陆地生态系统。因此,可以说SAD是氮的生物地球化学过程的人工强化。

表1　SAD细菌种类与特性

Table 1　Species and characteristics of SAD bacteria

菌属	微生物功能	微生物类型	适宜温度 T/℃	生长pH值	电子供体	电子受体	参考文献
Thiobacillus denitrificans	氧化还原态硫化物或单质硫	专性无机化能自养型菌	28~30	6.5~7.0	HS^-、S^0、$S_2O_3^{2-}$、FeS_2	NO_3^-、NO_2^-	[55-56]
Thiobacillus thiophilus	氧化硫代硫酸根	兼性厌氧革兰氏阴性菌	−2~30	6.3~8.7	$S_2O_3^{2-}$	NO_3^-	[57]
Thialkalivibrio nitratireducens	硝酸盐还原	硫酸盐弧菌	30	8~10.5	多硫化物、HS^-、$S_2O_3^{2-}$	NO_3^-	[58]
Sulfurimonas	硫氧化单胞菌	化能自养菌	15~35	6.5~8.5	S^{2-}、S^0、$S_2O_3^{2-}$、H_2	NO_3^-、NO_2^-	[49]
Sulfurimonas denitrificans	氧化硫化物	脱氮嗜硫单胞菌	22	7.0	HS^-、$S_2O_3^{2-}$	NO_3^-、NO_2^-	[59]
Sulfuricella denitrificans	反硝化作用	硫氧化自养菌	22	7.5~8.0	S^{2-}、S^0、$S_2O_3^{2-}$	NO_3^-、NO_2^-	[60]
Paracoccus	还原硝酸盐和亚硝酸盐	脱氮副球菌	22±1	7.5±0.3	S^{2-}、S^0、$S_2O_3^{2-}$、有机碳、H_2	NO_3^-	[61-62]
Thiomicrospira CVO	氧化硫化物还原硝酸盐	化能自养菌	5~35	5.5~8.5	HS^-、S^0、$S_2O_3^{2-}$	NO_3^-、NO_2^-	[63]
Ferritrophicum	2价铁氧化为3价铁	铁氧化细菌	6.4~19.2	7.4~8.1	Fe^{2+}、H_2、S^{2-}、S^0	NO_3^-	[64]

5　结论与展望

SAD技术在填料、反应器、耦合工艺等方面的研究取得了显著进步,成为污水绿色低碳脱氮的重要技术选择,且中国已在部分工程上得到了推广和应用。然而,SAD技术的工程化应用仍面临诸多限制:SAD工艺温度适应性需提高、反应器处理负荷亟待提升以及工程化工艺缺乏进一步创新等。以下几个方面未来可能成为SAD研究重点:

1)开发适应低温的SAD技术。研制抗低温SAD菌、设计适合低温运行的SAD工艺系统、开发耐低温的SAD填料载体,克服因低温导致SAD过程脱氮效率低的问题,提高SAD的温度适用范围。

2)提高硫自养反应器的处理负荷。加快传质,促进S^0的生物利用率,提高反应器单位体积处理负荷。此外,应用高效生物硫载体材料,如使用粒径较小的S^0颗粒或优化S^0颗粒表面结构,以及引入细胞外氧化还原介质或导电材料,都能提高反应器的处理负荷,这些思路还需要更多的研究验证。

3)SAD工艺的创新与应用。现有大多数研究采用SAD生物滤池的形式用于污水的深度脱氮,这增加了污水处理的流程且作用单一。未来研究应进一步缩短现有工艺,直接将SAD复合填料引入主

流水处理工艺中,探究SAD和异养反硝化细菌的协同脱碳机制,并开展工程应用研究。

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