安全与环保

剩余污泥电解氧化减量化性能研究

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摘要 进行了电化学氧化减量剩余污泥的研究,探究了不同电压、搅拌速度、电极材料以及电场方向对电解氧化污泥效果的影响。结果表明,在电压6 V、搅拌转速120 r/min、电极材料为石墨条件的优化下,7 h MLSS含量下降83.3%,SCOD提高至2.7 g/L;伏安特性曲线和电镜结果显示,电化学氧化高效作用于细胞破裂,以及可溶性COD(胞液)降解,表明电化学氧化对于剩余污泥降解具有显著效果,是一种前景广阔的污泥减量化技术。

关键词 剩余污泥;电化学预处理;性能优化
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随着我国城市化进程的加快,城市污水处理率逐年提高,但随之而来产生了大量二次污染物——剩余污泥。目前污泥减量化处理以厌氧消化为主,运行成本低、安全可靠而被广泛应用。但其处理时间长、设施占地大、产气率及产气量较低等瓶颈严重抑制其进一步发展[1]。此外,也有报道采用物理、化学、生物以及其联用的方法用于污泥减量[2-11]。但是,物理、化学技术高昂的处理成本亦严重限制该技术的实际应用[2]。因此,急需寻求一种经济、高效、环保的污泥减量化技术。

近几年,在生物处理系统中引入电化学技术进行产电、产氢和污染物降解等方面的研究逐渐成为环境与能源领域的一个新热点[12-14]。本研究通过构建剩余污泥电辅助厌氧消化反应器,优化电极材料与空间布置,获得优化污泥电化学预处理调控策略,并对减量机理进行了初步探讨。

1 实验部分

1.1 实验材料

实验所用活性污泥取自杭州某污水厂,基本参数:pH为6.6,固体质量分数0.7%,电导率110 mS/cm。

1.2 实验装置

电化学装置为有机玻璃制作的矩形反应器,反应器容积为1.5 L,电极正对面积为75 cm^2,板间距为6 cm;实验所用电源为直流稳压稳流电源,搅拌设备为恒温磁力搅拌器。

1.3 分析方法

pH采用精密pH计测定,混合液悬浮固体(MLSS)含量采用标准称量法检测,溶解性化学需氧量(SCOD)采用COD仪快速测定法检测;S420扫描/透射电镜(SEM)观察污泥表面,多通道CHI1040C电化学工作站测定伏安特性曲线。

2 结果与讨论

2.1 剩余污泥减量效果

MLSS单位电压溶出率S表明了MLSS的溶解的速度和程度,计算方法:

$$S=(\rho_0-\rho_t)/(U\rho_0)。$$

式中,ρ_0和ρ_t分别为MLSS原始和反应某时刻MLSS的质量浓度,U为电压。

图1为剩余污泥在6 V电压下的碳源转变过程。由图1可知,0~7 h时MLSS含量呈下降趋势,SCOD呈上升趋势;而7 h以后SCOD和MLSS含量均呈下降趋势,直至7 h时SCOD达到最高。原因是电化学氧化高效作用于细胞破裂,以及SCOD(胞液)降解,7 h之前细胞溶出速度快于有机物矿化速率,导致SCOD持续上升;7 h之后由于污泥中大部分细胞已经破裂溶解,氧化有机物速率开始高于细胞溶出速率,SCOD开始下降。

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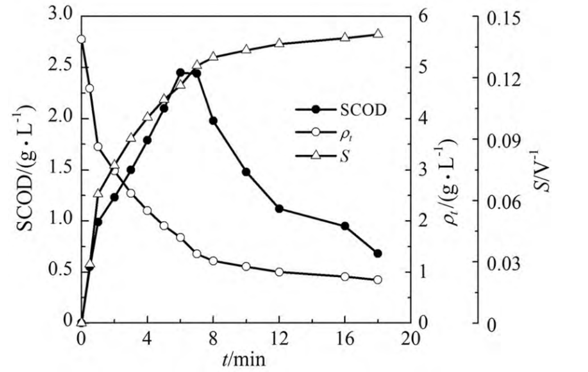
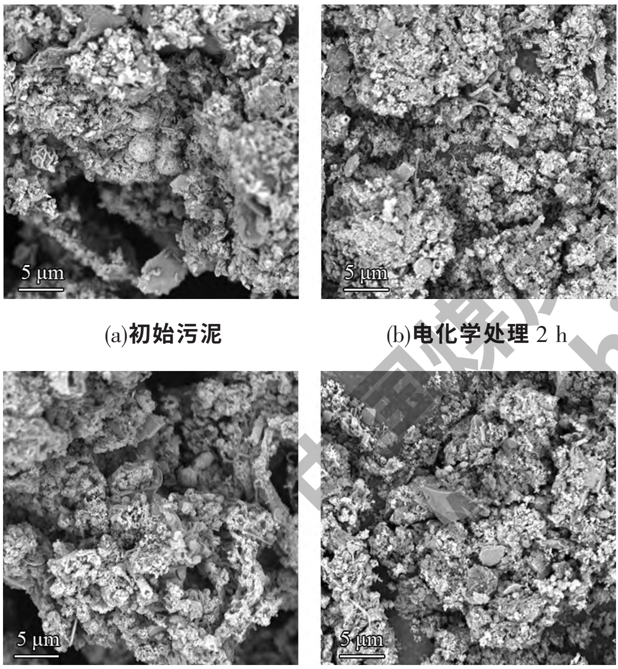


图 1　生物污泥电化学降解过程

Fig 1 The electrochemical degradation process of biological sludge

2.2　电化学作用机理分析

图 2 为原始和经过电化学作用后污泥的 SEM 照片。



(a)初始污泥　(b)电化学处理 2 h

(c)电化学处理 4 h　(d)电化学处理 7 h

图 2　扫描电镜图(8 000 倍)

Fig 2　Photo of SEM (×8 000)

由图 2 可知,原始剩余污泥细胞表现为完整、饱满，而经过电化学作用后基本已经不存在完整的细胞结构,并且混有少量石墨碎屑,由此进一步证明电化学作用对细胞破裂溶出具有显著作用。

图 3 为电化学作用前及作用后的线性伏安特性曲线,用于电极表面反应过程。

由图 3 可知,在电化学作用前细胞形态完整,与电解液完全分离，此时电极表面没有发现任何氧化还原过程,由此说明细胞破裂溶出、破坏结构之后开始氧化细胞内的有机物。经过电化学作用后,电极表面出现大量氧化还原峰,且氧化还原面积显著扩大,

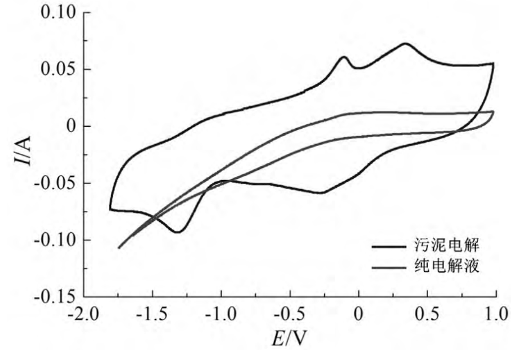


图 3　电化学作用前后伏安特性曲线

Fig 3　Characteristic curve of volt-ampere before and after electrochemical

这充分说明水体中含有大量的细胞溶出有机物进行氧化反应进行降解。综上可知,电化学作用先对细胞进行破碎直至细胞液溶出，然后开始作用于溶出有机物的降解矿化。

2.3　电化学作用条件优化

由上述可知,7 h 之前污泥细胞溶出速度快于有机物矿化速率,该过程成本较高,且不利于后续污泥发酵处理,因此电化学时间停留在 7 h 以前。电化学主要影响因素有电压、电极材料、电场方向和搅拌速度。

2.3.1　电压

图 4 和图 5 分别为不同电压对 MLSS 含量和 SCOD 的影响。

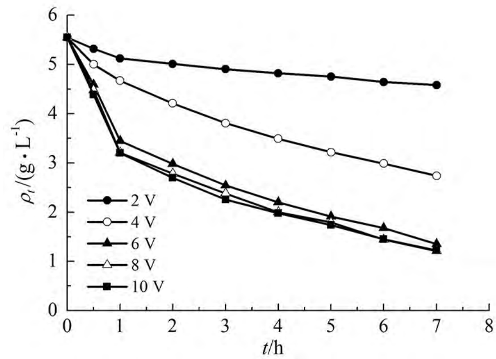


图 4　电压对 MLSS 含量的影响

Fig 4　Effect of voltage on MLSS content

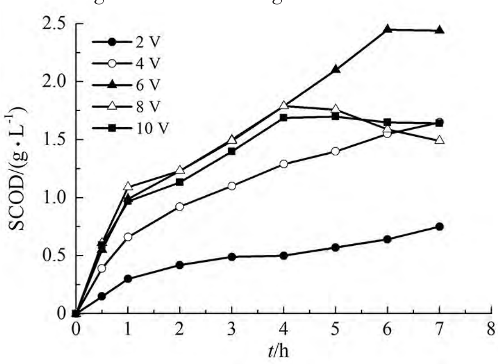


图 5　电压对 SCOD 的影响

Fig 5　Effect of voltage on SCOD

图 4 和图 5 可知，电压对 MLSS 含量和 SCOD 影响很大，随着电压的增大(2~10 V)，细胞破裂速率显然加快，MLSS 的溶解速率和 SCOD 的生成速率均有明显的提高。电压达到 6 V 及以上后，SCOD 在 4 h 以后反而呈下降的趋势，原因是在外加 6 V 以上电压之后，细胞 MLSS 的质量浓度低于 2 g/L，导致细胞破裂后产生得 SCOD 速度慢于 SCOD 氧化速率。从 SCOD 增加量的角度来看，6~12 V 电压条件下差距并不明显，所以实验的适宜的电压是 6 V。

2.3.2 搅拌

搅拌可以使剩余污泥在反应器内均匀分布，并加大接触电极表面的几率从而增大氧化还原过程的场所。图 6 为剩余污泥在 pH 为 7.0、电压为 6 V 的条件下，MLSS 含量和 SCOD 在不同搅拌转速下的降解过程。

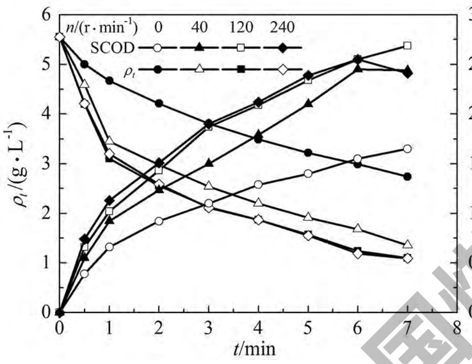


图 6 不同搅拌强度对 MLSS 含量和 SCOD 的影响

Fig 6 Effect of agitation rate on MLSS content and SCOD

由图 6 可知，不同搅拌强度对 MLSS 含量和 SCOD 的影响很大，MLSS 的溶解速率和 SCOD 的生成速率均有明显的提高，且搅拌转速在 0~120 r/min 时，MLSS 的溶解速率和 SCOD 的生成速率随着搅拌转速的增加而增大。搅拌时电解质分布均匀，电解表面积增大，电解速率增加；但是，当搅拌转速分别为 120 r/min 和 240 r/min 时，2 者相差并不明显，原因是在转速达到 120 r/min 左右时溶液内电解质分布已经足够均匀。所以从节约能源的角度出发，适宜搅拌速度为 120 r/min。

2.3.3 电极材料

电极材料是反应器最主要的组成，电极影响效果的作用体现在电极内阻、表面积以及生物兼容性，符合这 3 项性能的电极可以有效提高电极与微生物之间的反应。图 7 为剩余污泥在 pH 为 7.0、电压为 6 V 的条件下，MLSS 含量和 SCOD 在不同电极材料中的降解过程。

不同电极材料的导电性能排列依次为钛/二氧

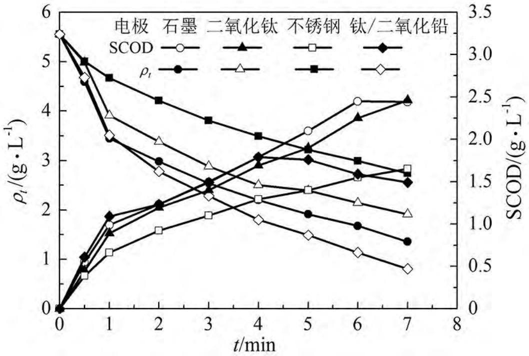


图 7 不同电极材料对 MLSS 含量和 SCOD 的影响

Fig 7 Effect of different electrode material on MLSS content and SCOD

化铅>石墨>二氧化钛>不锈钢。由图 7 可知，以钛/二氧化铅作为电极材料时，在 4 h 以后 SCOD 反而下降，原因是 4 h 后钛/二氧化铅电极的反应器内开始以氧化溶解性有机物为主，而其他 3 种电极材料的反应器仍是以污泥细胞溶解为主。这说明钛/二氧化铅导电性能最好，反应速率最快；但是从 SCOD 增加量的角度来看，钛/二氧化铅电极与石墨电极相差并不明显，所以从经济的角度出发，适宜的电极材料是石墨电极。

2.3.4 电场

图 8 为在 pH 为 7.0、电压为 6 V 的条件下，MLSS 含量和 SCOD 在不同电场布置下的降解过程。

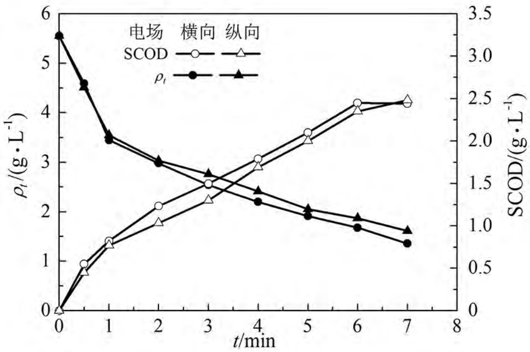


图 8 水平电场和垂直电场对 MLSS 含量和 SCOD 的影响

Fig 8 Effect of horizontal electric field and vertical electric field on MLSS content and SCOD

由图 8 可知，MLSS 含量随电解时间的增加呈总体下降的趋势，而 SCOD 则呈总体上升的趋势。这说明在外加电压条件下污泥细胞不断破碎溶出，使得可溶性有机物不断增加；而不同电场布置(水平电场或者竖直电场)对 MLSS 含量和 SCOD 的影响并不明显，原因是重力对电解速率的大小并无明显影响。

3 结论

1)电化学预处理污泥减量效果显著。剩余污泥在

电化学氧化还原作用下细胞迅速破碎，细胞液溶出，SCOD 急速上升，同时电化学作用对 SCOD 具有高效降解能力。

2)剩余污泥细胞结构首先在电化学作用被完全破坏，细胞液流出致使溶液电解液电导率急速上升，而后电化学开始作用于溶出有机物的降解。

3)电化学处理优化电压为 6 V、搅拌转速为 120 r/min，阴阳电极均选取石墨作为基底材料。在此优化条件下，经 7 h 反应后，MLSS 的质量浓度下降 83.3%，SCOD 提高至 2.7 g/L，有利于污泥生物减量化效率的进一步提高。

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Production and Reaction of Lithium Aluminium Hydride

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Abstract:The main point of this report was introducing the normal way, high-pressure way and $NaAlH_4$ way of production of $LiAlH_4$, concluding and listing the examples of reduction reaction about $LiAlH_4$ with halide, carboxylic acid, ester, aldehyde, ketone, cyanogroup, special carbon-carbon double bonds and some uses of $LiAlH_4$. By comparing different instances, pointed out that the lithium aluminium hydride played different role in chemical industry field. And because of the excellent capacity of educing, it was important to design reasonable condition of reaction to achieve the biggest effect of $LiAlH_4$ in production, which was very important in the production and scientific research.

Keywords:aluminum hydroxide; preparation; reduction reaction

Carbon Trading and Carbon Asset Management in Chemicals Industry in China

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Abstract: This paper presented a summary of carbon trading market in China, the definition and the category of carbon asset, core content and offset mechanism of carbon quota asset and project asset management, and carbon trading rule by example of Beijing carbon trading practice, this paper also proposed that managements in chemical companies under carbon emission credit total quantity control should upgrade the consciousness of low carbon management, accordingly build up carbon asset management organization structure and management tool, analyze and study market operation mechanism of carbon trading market, comprehensively calculate enterprise´s cost of conforming international regulation, flexible use offset mechanism, optimize carbon asset management, use market leverage, take opportunity effect, reduce enterprise´s cost of emission reductions, and elevate enterprise´s competiveness.

Keywords: carbon asset; carbon asset management; carbon emission quotation; Chinese Certified Emission Reduction; offset mechanism; suggestion

Performance Study on Excess Sludge Reduction by Electrolytic Oxidation

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Abstract: The research offered a new-type way to reduce the excess sludge in electrochemical oxidation system. The influence of voltage, agitation rate, electrode material and electric field direction on the effect of sludge electrolytic oxidation were Investigated. The results showed that under the conditions of 6 V voltage, 120 r/min agitation rate and graphite electrode material, the mixed liquor suspended solid (MLSS) content declined 83.3% and the soluble chemical oxygen demand (SCOD) increased 2.7 g/L. The characteristic curve of volt-ampere and the scan electron microscope (SEM) photo showed that the electrochemical oxidation could dissolve cell and degrade SCOD efficiently, which indicated that the electrochemical oxidation was remarkable to excess sludge reduction. It was a promising technology for sludge reduction.

Keywords: excess sludge; electrochemical pretreatment; efficiency optimization

Relationship between Physical and Chemical Properties of Materials and Mechanical Damage of Polyethylene Gas Pipe

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Abstract: The paper described the relationship between the physical and chemical properties of raw materials and mechanical damage of polyethylene gas pipe, then pointed out that it is essential for the healthy development of polyethylene gas pipe to establishing and improving relevant standards. Density and melt flow rate affected the mechanical damage of polyethylene gas pipe indirectly and the material mechanical damage performance was strongly affected by the relative molecular weight distribution of raw materials, the distribution between different molecular weight level of comonomers and sequence distribution of comonomer in molecular chain. The uniformity and crosslinking degree in polyethylene crosslinking process had major impact on the performance of polyethylene gas pipe. The excessive deformation or buckling problem of polyethylene pipe caused by ring stiffness under some