

两相颗粒污泥 UASB 结合离子交换工艺及模型化研究

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摘要 运用两相颗粒污泥 UASB 反应器结合离子交换 (TP-UASB-AE) 新工艺处理配制葡萄糖废水取得了容积有机负荷达 $62 \text{ g}/(\text{L} \cdot \text{d})$, COD 去除率为 91.5% 的高效能和过程高稳定性。对 TP-UASB-AE 工艺的各个单元均建立了反应器级的控制数学模型, 并实现了整体工艺的系统模型化控制, 其系统模型化计算结果与实验结果的平均相对误差为 2.2%。运用系统控制模型可对工艺过程进行精确和方便的调节, 也是工程放大设计和自动化控制的基础。

关键词 废水处理, 两相厌氧消化, UASB, 颗粒污泥, 离子交换, 数学模型。

可溶性碳水化合物废水的两相厌氧消化虽然比单相厌氧消化有更好的过程稳定性^[1], 但产甲烷相出水中的 HCO_3^- 是随出水排掉的, 而需另加碱基于产酸相中以部分中和进入产甲烷相的有机酸, 否则仍然会导致产甲烷相发生过程不稳定。为解决这个问题 J. H. Thiele 和 J. G. Zeikus^[2] 于 1987 年提出了两相厌氧结合离子交换的新概念, 设想在产酸相和产甲烷相之间加入 2 个离子交换单元, 以充分利用产甲烷相出水中的末端产物 HCO_3^- , 中和产酸相出水中之 H^+ 。但他们对此设想仅进行了初步的模拟实验, 未能实现此设想。本研究在两相颗粒污泥 UASB 工艺研究的基础上, 借鉴了两相厌氧结合离子交换工艺设想的优点, 提出了两相颗粒污泥 UASB 结合离子交换 (简称 TP-UASB-AE) 新工艺, 以期进一步提高厌氧消化的效能和稳定性。

1 材料和方法

基质: 葡萄糖 500 g, $(\text{NH}_4)_2\text{CO}_3$ 30 g, KH_2PO_4 10 g, 加自来水至 2000 ml, 贮于冰箱中用时稀释。

实验温度: 35°C 。

分析方法: COD: 重铬酸钾法^[3]; 葡萄糖: 3, 5-二硝基水杨酸法^[4]; pH: pH-酸度计。挥

发性有机酸 (VFA): 离子排斥色谱法^[4]; 流态示踪实验示踪剂 Ni^{2+} ; 采用 3200 型原子吸收分光光度计测定^[4]。

实验装置和流程: 见图 1。

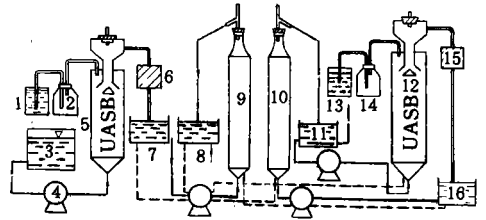


图 1 TP-UASB-AE 工艺实验流程图

3、7、8、11、16: 贮槽 1、2、13、14: 气体收集系统 4: 恒流泵 6、15: 过滤器 9、10: 离子交换柱 12: 产甲烷 UASB 5: 产酸 UASB

TP-UASB-AE 工艺包括 4 个单元: 产甲烷颗粒污泥 UASB (直径 5 cm, 0.75 L), 产酸颗粒污泥 UASB (直径 4 cm, 0.375 L), 2 个 717 阴离子交换树脂柱 (直径 3 cm × 高 45 cm) 及附设的过滤器装置。其工作流程如图 1 所示, 贮槽 3 中的配制葡萄糖废水经产酸 UASB 处理并经过滤后进入贮槽 7, 此富含挥发性有机酸 (VFA⁻) 的产酸相出水入初始为 HCO_3^- 型式的离子交换柱 9, 其中的 VFA⁻ 被交换结合在树脂

上,而 HCO_3^- 被交换至液相随离子交换柱9的出水至贮槽8,此无 VFA^- 的出水即可排入环境;贮槽16中经过滤后的产甲烷UASB出水(富含 HCO_3^-)通入 VFA^- 型式的离子交换柱10, HCO_3^- 将 VFA^- 交换至液相随离子交换柱10出水至贮槽11,此富含 VFA^- 的离子交换出水即可作为产甲烷相进水通入产甲烷UASB反应器。当完成一个工作周期后,离子交换柱9与10相互切换工作位置(2个离子交换柱进水管线由实线切换为虚线),进行下一周期的工作。2个离子交换柱的工作过程也是它们的相互自再生过程,如此往复进行周期性切换,即可使工艺连续进行。

2 结果和讨论

2.1 TP-UASB-AE 工艺运行效能的研究

以配制葡萄糖废水为基质的TP-UASB-AE工艺运行180 d的实验结果如图2。

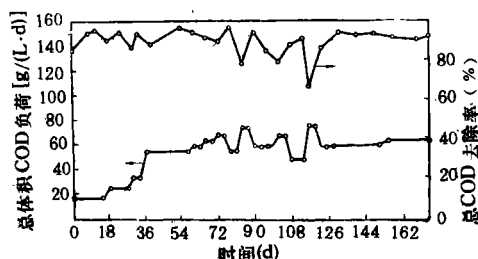


图2 TP-UASB-AE 总体工艺运行结果

比较图2和以往的研究^[4,5]可以看出,TP-UASB-AE工艺对配制葡萄糖废水的稳态运行处理负荷达 $62 \text{ g}/(\text{L} \cdot \text{d})$,COD去除率为91.5%,处理能力明显高于单相和常规两相厌氧。其主要原因为:

(1) 本工艺充分利用了产甲烷相出水中富含的末端产物 HCO_3^- ,避免了低pH的产酸相出水直接进入产甲烷相,故比常规厌氧具有更高的过程稳定性;

(2) 本工艺的产酸UASB反应器中形成了高效能的产酸颗粒污泥床,具有很高的产酸速率和酸化率;由于离子交换单元的加入使工艺的出水排放是在产酸相,产甲烷相可在较高基

质浓度下操作而不直接影响出水处理效果,加快了生长较慢的产甲烷菌的代谢速率;

(3) 由于实现了整体工艺的系统模型化,因而就可以对TP-UASB-AE的操作匹配运行进行精确和方便地控制。

2.2 TP-UASB-AE 工艺过程的数学模型化

2.2.1 UASB反应器的数学模型

UASB颗粒床反应器由于其污泥层区和沉降区的污泥浓度相对污泥床区很低,故可将此反应器系统简化为固定化床系统来进行数学处理。采用轴向离散模型^[6]描述颗粒床的流态,在得到离散数 $1/P_e$ 后,采用有反应项的轴向离散模型^[6]建立上流式UASB颗粒床的稳态数学模型。

2.2.1.1 流体流动模型

通过对颗粒污泥床的微分物料衡算得流态的轴向离散模型:

$$\begin{aligned} \frac{\partial c}{\partial \theta} &= (E_z/u \cdot L) \cdot \frac{\partial^2 c}{\partial Z^2} - \frac{\partial c}{\partial Z} \\ &= (1/P_e) \cdot \frac{\partial^2 c}{\partial Z^2} - \frac{\partial c}{\partial Z} \end{aligned} \quad (1)$$

当采用阶跃输入时,其初始和边界条件是:

$$\begin{aligned} c(Z, 0) &= 0; \quad dc/dZ(1, \theta) = 0; \\ c(0, \theta) &= 1/u + (1/P_e) \cdot \partial c / \partial Z \end{aligned}$$

式中, $P_e = u \cdot L / E_z$,称为Peclet准数; L :颗粒污泥床最大高度; u :液体流速; E_z :扩散系数; c :无量纲示踪剂或基质浓度; θ :无量纲时间; Z :无量纲颗粒污泥床高度。

对式(1)采用有限差分结合韦伯斯特法^[7,8]计算机数值求解。求解结果为停留时间分布曲线(RTD曲线)。运用试差法即可确定反应器某一状态下的 P_e 数。

2.2.1.2 产甲烷UASB颗粒污泥床数学模型

确定了某状态下的 P_e 数后,通过去除式(1)中的非稳态项和加入基质消耗项得产甲烷UASB颗粒污泥床的数学模型:

$$\begin{aligned} \frac{d^2 c}{dZ^2} - P_e \cdot \frac{dc}{dZ} - K_{\max} \cdot \tau \cdot X \\ \cdot P_e \cdot c / (K_s + c_0 \cdot c) = 0 \end{aligned} \quad (2)$$

$$c - 1/P_e \cdot dc/dZ = 1 \quad (Z = 0);$$

$$dc/dZ = 0 \quad (Z = 1)$$

$K_{\max}$: 最大比基质反应速率 $[\text{g COD}/(\text{g VSS} \cdot \text{d})]$;

K_s : 半饱和常数; c_0 : 进水基质浓度 $[\text{g COD}/\text{L}]$;

X_i : 菌体浓度(gVSS/L); τ : 进水在污泥床中的平均停留时间, 其它量同式(1)。

采用有限差分结合牛顿拉福森法^[7]计算机数值求解, 求解结果为基质通过污泥床后的去除率。

2.2.1.3 产酸 UASB 颗粒污泥床的数学模型

模型推导类似于产甲烷 UASB, 得产酸 UASB 数学模型:

$$\begin{cases} d^2c/dZ^2 - P_e \cdot dc/dZ - \\ \quad K_{\max} \cdot \tau \cdot X \cdot P_e \cdot c / \\ \quad (K_i + c \cdot c_0) K_i / [K_i + \\ \quad c_0(1 - c)(1 - 1.42Y_g)] \\ c - 1/P_e \cdot dc/dZ = 1 \quad (Z = 0) \\ dc/dZ = 0 \quad (Z = 1) \end{cases} \quad (3)$$

K_i : 抑制常数(mgVFA-COD/L); Y_g : 产酸菌体产率(g VSS/gCOD); c_0 : 进水基质浓度(mgCOD/L); 其它量同式(2)。

求解方法同式(2), 求解结果为基质通过床层后的转化率。

2.2.2 离子交换单元过程的数学处理

2.2.2.1 VFA⁻溶液交换洗脱 HCO₃⁻ 型式离子交换树脂的柱内过程

由于离子交换过程是由传质过程控制的^[9], 采用总传质系数模型^[9]对其描述:

$$\begin{cases} u \cdot \partial c / \partial l + \epsilon \cdot \partial c / \partial t + \rho \cdot \partial q / \partial t = 0 \\ \partial q / \partial t = K_o \cdot (c - c^*) \\ c^* = q \cdot c_o / q \cdot (1 - K) + q_o \cdot K \end{cases} \quad (4)$$

u : 柱截面积的液体流速(cm/min); c : 流动相浓

度(mmol VFA/L); l : 柱的轴向距离(cm); t : 时间(min); ϵ : 床层空隙率; q : VFA 在固定相的浓度[mmol/g(干基)]; ρ : 树脂视密度(干)(g/ml); K_o : 总传质系数; c^* : 与树脂相中 VFA⁻浓度 q 相平衡的液相 VFA⁻浓度(m mol/L); q_o : 树脂相中的饱和 VFA⁻浓度[mmol/g(干)]; K : 选择性平衡常数; c_o : 进水 VFA⁻浓度。

此方程组采用有限差分结合叠代法^[7], 计算机数值求解, 求解结果为 VFA⁻在离子交换柱出水中的透过曲线。

2.2.2.2 HCO₃⁻ 溶液洗脱交换 VFA⁻型式树脂的柱内交换过程

采用交换区域移动法^[10]建立数模:

$$t = H/u \cdot (q/c_o + \epsilon) \quad (5)$$

H : 树脂层最大高度(cm); q : 离子交换树脂中 VFA⁻的浓度 mmol/ml(视); c_o : 进水 HCO₃⁻ 浓度 mmol/ml; 其它量同式(4)。

运用式(5)可以求出一个置换周期出水中的理论 VFA⁻浓度。

2.2.3 TP-UASB-AE 整体工艺模型化控制及拟合

按照工艺流程, 将每个单元的数学模型顺序联接计算即可控制过程操作使整个工艺的过程控制系统模型化。

从表 1 可计算出总 COD 去除率的实验与模型计算值的相对平均误差=2.2%。故此工艺的一系列模型化描述基本符合实验结果。

表 1 TP-UASB-AE 工艺匹配运行的模型计算与实验结果

实 验 编 号	1	2	3	4	5	6
进水基质浓度(mgCOD/L)	12500	12500	12500	12500	19000	19000
总有机负荷[gCOD/(L·d)]	53.5	58.0	62.4	66.8	58.0	66.8
总水力停留时间(h)	5.63	5.19	4.82	4.50	7.89	6.85
实验值[总 COD 去除率(%)]	96.6	93.9	91.5	89.2	87.5	79.8
计算值[总 COD 去除率(%)]	98.3	96.7	93.8	89.7	89.4	82.4

2.2.4 模型分析、控制及其应用意义

对工艺过程的精确控制和调节具有实践意义。以表 1 中实验编号 1 为例, 操作参数如下: 产酸相进水流量=4.8 L/d; 离子交换周期=

360 min; 产甲烷相流量=4.375 L/d。当进水浓度变为 19650 mgCOD/L 时, 为维持总 COD 去除率不变, 通过系列模型计算确定出各匹配单元新的操作参数为: 产酸相进水流量=2.42

L/d; 离子交换周期=485 min; 产甲烷相流量=3.32 L/d。

可确定产酸颗粒床与产甲烷颗粒床的最佳体积比。例如, 已知进水葡萄糖浓度=12500 mg COD/L, 产酸反应器负荷=560 gCOD/(L·d), 取产酸颗粒污泥床体积为 0.05 L, 规定工艺总 COD 去除率为 95%。通过系列模型推导计算得: 所需产甲烷颗粒污泥床的体积=0.275 L, 产酸颗粒床体积/产甲烷颗粒床体积=1/5.5。

当然, 工业化实用最佳体积比还要综合考虑运行经济性 & 操作方便等而定。

2.3 离子交换单元和辅助过滤单元的可行性

采用离子交换柱数学模型结合实验流出曲线试差法评价离子交换树脂有效工作交换容量的损失速率。

从表 2 可以看出: 离子交换树脂有效工作交换容量的损失速率是缓慢的。

表 2 工艺运行过程中离子交换树脂有效工作交换容量的损失情况

时间(月)	0	1	3	6
有效工作交换容量 [mmol/g(干)]	3.11	2.8	2.68	2.5
损失速率[mmol/g(干)·月]		0.31	0.06	0.06
累计损失百分比(%)		9.96	13.8	19.6

长时间的运行结果表明: 辅助性多层滤布过滤效果良好, 离子交换柱未发生堵塞和交换效能不良。

3 结论

(1) 运用 TP-UASB-AE 工艺处理配制葡萄

糖废水具有很高的处理负荷[62 gCOD/(L·d)]和 COD 去除率(91.5%), 并具有很好的过程稳定性。对于此类含 SS 少的可溶性碳水化合物废水, 运用 TP-UASB-AE 工艺优于常规两相和单相厌氧工艺。

(2) 系统模型化对工艺过程的精确控制、调节、预测和优化具有实用价值, 为实现工艺过程的自动化控制提供了基础, 同时对工程放大设计也提供了一个研究方法。

(3) 离子交换柱单元在本工艺中的应用具有相互切换自再生和长时间内无需特殊再生的优点。

(4) 离子交换柱体积为生物反应器体积的 1/100 时仍可正常匹配^[2], 工程应用中可使离子交换柱体积比生物反应器体积小得多, 故与常规两相厌氧相比, 工程上的投资增加不多。

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Abstracts

Chinese Journal of Environmental Science

Effects of PCBs on the Electrolyte Balance in Blood of Crucian Carp. Xi Zhiquan et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 1-3
The effects of PCBs exposure on the concentrations of electrolytes (sodium, potassium, calcium, magnesium) in blood plasma of the crucian carp were examined. In the Crucian Carp, the plasma sodium concentration increased significantly during the exposure to an aqueous PCBs solution and the plasma sodium concentration increased as the concentration of PCBs increased. The plasma concentration of potassium decreased during the exposure to PCBs, and the plasma potassium concentration decreased as the concentration of PCBs increased. The Plasma concentrations of calcium and magnesium did not show any clear patterns.

Key words: PCBs, blood electrolyte balance, Crucian Carp.

QSAR of Substituted Phenol Derivatives. Zhang Daren (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 4-6

The molecular surface areas of 29 substituted phenol with 7 various substituents were calculated. In addition to molecular surface area and OH group's surface area, the substituent equivalent was pointed out to be necessary to be used as a desorptive variable. Using the three Parameters, a regression analysis was performed for the Microtox^R toxicities of above mentioned compounds, giving a meaningful regression equation with a correlation coefficient of 0.90. If 4-cyanophenol of them were regarded as an outlier and deleted from the above compounds in question, then the correlation coefficient was up to 0.94. The results show that these parameters were important in predicting the toxicity of some compounds.

Key words: substituted phenol derivatives, molecular surface area, substituent equivalent, Microtox^R.

Toxicities of Nitroaromatic Compounds to *Scenedesmus obliquus* and Toxic Symptoms. Liu Jingling et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024): *Chin.*

J. Environ. Sci., **16**(2), 1995, pp. 7-10

By using an OECD standard method for algal growth inhibition test, the toxicities (48 h, EC₅₀) of 25 nitroaromatic compounds to *Scenedesmus obliquus* were determined. their toxicities ranked in a decreasing order were: dinitrochlorobenzene > dinitrobenzene > dinitroaniline > dichloronitrobenzene ≡ dinitrotoluene > nitro-bromobenzene ≡ nitrochlorobenzene > nitrotoluene ≡ methoxynitrobenzene ≡ nitrophenol > nitroaniline > nitrobenzene. The toxicities of the compound to the algae varied depending on the concentrations and kinds of the compounds. Under the microscope (400 times), 4 kinds of toxic symptoms were observed, including the inhibition to the filial spore release; the separation of protoplasm form wall of cell; the disintegration of nucleus and organs; and the destruction of protoplast. The results show that the algae growth inhibition test would have a prospect of wide application in water quality monitoring and pollution control.

Key words: algal inhibition test, nitroaromatic compounds, *Scenedesmus obliquus*, EC₅₀, toxic symptoms.

Study on the Process and Modelling of Two-phase Granular Sludge UASB Reactor coupled with Anionic Exchange Units. Yang Hong et al. (Dept. of Bioscience and Biotechnology, Shanghai Jiao Tong University, 200030): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 11-14

The study on a novel process of Two Phase Granular Sludge UASB Reactor Coupled with Anionic Exchange Units (TP-UASB-AE) using glucose as a substrate showed that a very high volume loading rate [COD, 62 g/(L · d)] was reached when COD removal efficiency was 91.5%. A control mathematic model for each of TP-UASB-AE units was established separately. The whole TP-UASB-AE system was modelled through the combination of anionic exchange colume models and UASB models. The mean relative error between the system model calculating results and experimental results was 2.2%. The whole process can be exactly and conveniently controlled by using the system control model. It also provides a foundation for engineering scale-up and automatic control.

Key words: wastewater treatment, two-phase granular sludge, UASB, mathematic model, anionic exchange.

Study on the photodegradation of Dyes in Aqueous Solution over a Ag-loaded TiO_2 Catalyst. Jiang Weichuan et al. (Dept. of Chemistry, Zhejiang University, Hangzhou 310027); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 15–18

Photodegradation of dyes in aqueous solution was investigated by irradiating with a 300 watts high pressure mercury lamp and using silver loaded titanium as a catalyst. The results show that the Ag loaded TiO_2 had a higher catalytic activity than a pure TiO_2 . An aqueous solution containing 50 mg/L of dye could be decoloured over a Ag loaded TiO_2 catalyst with a 40–60 min irradiation, which was 15–40 min less than that in the case of using a pure TiO_2 as a catalyst. The effects of temperature, pH, photo-intensity and quantity of catalyst agent were also investigated.

Key words: silver, catalyst, photodegradation, dye.

Radon Levels in the Regional Environment of Gejiu, Yunnan, and Their Relationship to the Geological Features. Lu Wei et al. (Tianjin Institute of Geology and Minerals, Tianjin 300107); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 19–22

By using a SSNTD method, the study on the concentrations of radon and its distribution and transportation patterns in the regional environment of Gejiu was carried out, during the period of 1990–1992, through an environ-geological field survey and the soil and indoor monitoring at selected sites, with 479 data obtained. The results show that, although uranium or thorium ores had not yet discovered in this area, the soil radon levels were generally higher than the world average of soil radon in the earth's crust. In the residential houses located on geological faults, there was an average indoor radon level of up to $471.9 \text{ Bq} \cdot \text{m}^{-3}$, much higher than the average radon level measured in some parts of this country in recent years. In contrast to the results reported in domestic and international literatures, the indoor radon levels in this area were higher in summer and lower in winter and were positively correlated to the number of building storeys, with the indoor radon level at a top storey being as much as 2.70 times that at a ground storey. This could be related to the environmental and geological factors in Gejiu area. It was suggested that

the measures for preventing radon from causing a cancer should be taken, including the construction of residential houses at a distance far away from the geological faults, and the prevention of ascending air streams with radon radiation from the escape into the residential rooms.

Key words: Gejiu area, radon level, soil, indoor.

Study on the Combined Bacteria-Emulsion Process for Coal Desulfurization. Chen Min, Xu Fuming et al. (School of chemical Eng., Nanjing Univ. of Science and Technology, Nanjing 210094); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 23–26

A study was made on the principles of a combined bacteria-emulsion process for removing sulfur from coal, the species of bacteria used for this purpose, and the operation conditions of this process. The results show that a combination of emulsification technology with microbial desulfurization technology has substantially improved the efficiency of desulfurization. During a period of 2 or 3 days, 53.2% of pyrite were removed from coal at a total desulfurization rate of 32.7%. The sulfur removal varies with the changes in the size of coal particle and the conditions of reaction, with a maximum removal of up to 47% in 2 days.

Key words: coal desulfurization, microbial desulfurization, combined bacteria-emulsion, desulfurization process.

Study on Desulfuration Characteristics of Limestone with Thermogravimetric Analysis Technique. Liu Qianxin, Ni Xiaofen et al. (Thermoenergy Eng. Research Institute, Southeast Univ., Nanjing 210008); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 27–30

A thermogravimetric analyzer was used in studying the desulfuration reaction of limestones from Jiawang, Changshan and Tongshan in Xuzhou city. The effects of limestone type, desulfuration temperature, the concentration of SO_2 and limestone particle size on sorbent conversion rate were investigated; the values of constant K of chemical reaction velocity and the coefficient b of reaction velocity were calculated. A particle size of less than 0.5 mm gave a value of K in the range of $9.4 \times 10^{-4} - 22 \times 10^{-4} \text{ ms}^{-1}$; a particle size between 0.5–1.0 mm, $b = 1254 \text{ min}^{-1}$; and a particle size between 1.0–2.0 mm, $b = 1103 \text{ min}^{-1}$.

Key words: thermogravimetry, limestone, desulfuration.