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目 次

BP 网络框架下 MODIS 气溶胶光学厚度产品估算中国东部 $PM_{2.5}$ 郭建平,吴业荣,张小曳,李小文(北京市近地层颗粒物浓度与气溶胶光学厚度相关性分析研究	817)
一样海峰, 辛金兀, 张ズ煜, 土跃思, 刘子锐, 陈传雷(气象因素对长三角背景地区甲烷浓度的影响分析————————————————————————————————————	826) 835)
密闭化填埋作业条件下的场内恶臭污染分布情况与分析	842) 849)
2000~2010年大鹏湾颗粒有机物的年变化相年际变化	857) 864) 874)
漳卫南运河流域非点源污染负荷估算及最佳管理措施优选	882) 892)
几龙江口湿地植物凋洛物对沉枳物有机质赋仔的贡献····································	900)
修复达标土壤回填対地ト水环境影响的层次化评估方法应用研究	914) 919)
城市污水处理厂及具受纲水体中 5 种典型 PPCPs 的赋仔特征和生态风险	927) 933) 943)
膜生物反应器处理工业废水中膜污染及膜过滤特性研究····································	950)
限生物反应器处理工业废水中限污染及限过滤符性研究 泡率红, 采素杯, 张培师, 三业球, 刘锐, 陈旨车(γ -Al Q 3 负载磷钨酸催化强化电化学法处理水中酸性大红 3R 的研究	955) 962) 968)
风快 化相列介油 及小 UADD-SF SDIT-MAI 又是工人工以则几	919)
连续流心下以城巾乃小培养好氧颗粒石泥及颗粒符性研究 午妹,校百川,宏作黑,刈壬峰,宏家铭,王聪,周开升(乙酸/丙酸作为 EBPR 碳源的动力学模型研究(Ⅱ)——模型的建立 张超,陈银广(乙酸/丙酸作为 EBPR 碳源的动力学模型研究(Ⅱ)——动力学模拟 张超,陈银广(986) 993) 998)
乙酸/丙酸作为 EBPR 碳源的动力学模型研究(Ⅲ)——模型的应用 ····································	1004)
正竣流念下以城巾乃水培养好氧颗粒行泥及颗粒特性研究 ······ · · · · · · · · · · · · · · ·	1026)
层次化健康风险评估方法任本污染场地的应用及效益评估	1034) 1044)
大金山岛土壤重金属污染评价及相关性分析 ·······················程芳,程金平,桑恒春,于金莲,席磊,皮帅帅(典型有色金属矿山城市小河流沉积物重金属形态分布及风险评估 ·············李如忠,姜艳敏,潘成荣,陈婧,徐晶晶(1062) 1067)
典型有色金属矿业城市零星菜地蔬菜重金属污染及健康风险评估 ········· 李如忠,潘成荣,徐晶晶,陈婧,姜艳敏(城市表层土壤磁化率与重金属含量分布的相关性研究 ··················	1076) 1086)
+ 大奶润序泥屋树上涨III 财灶料III 农	1101
三峡库区澎溪河底泥及消落区土壤磷的形态及吸附特性研究····································	1107) 1114)
至認為保險。相信与磷酸的符任研究 三峡库区澎溪河底泥及消落区土壤磷的形态及吸附特性研究 一球市的 X-100 在黄土上的吸附行为及影响因素 一切,一切,一切,一切,一切,一切,一切,一切,一切,一切,一切,一切,一切,一	1120) 1129)
太湖沉积物中多溴联苯醛和类— 呢 英多氯联苯的水平垂直分布 ————————————————————————————————————	1136) 1142)
柴油轿车颗粒多环芳烃的排放特性····································	1150) 1156)
固体添加剂对污泥焚烧过程中重金属迁移行为的影响 ····································	1166) 1174)
Cr ⁶⁺ 生物可利用度检测的微生物全细胞传感器 CB10 的构建及其响应特征 ········ 侯启会,马安周,庄绪亮,庄国强(反硝化脱硫工艺中微生物群落结构及动态分析 ····································	1181) 1190)
青海省西宁市与天峻县大气中得克隆与十溴联苯醚的水平与来源 何畅,金军,马召辉,王英,扎西卓玛,马丽花(太湖沉积物中多溴联苯醚和类二噻英多氯联苯的水平垂直分布 马召辉,金军,亓学奎,王英,姜霞,何松洁,李明圆(典型电器工业区河涌沉积物中有机污染物特征分析 "理不强,周舟,胡志远,楼秋明(机械炼焦过程生成飞灰中多环芳烃分布特征研究 华玲,彭林,刘效峰,白慧玲,张建强(万泥下化床与芦苇床稳定化污泥中多环芳烃的含量比较 崔玉波,孙红杰,冉春秋,李金凤,谢瑶(百体添加剂对污泥焚烧过程中重金属迁移行为的影响 "崔玉波,孙红杰,冉春秋,李金凤,谢瑶(传造废砂的环境毒性研究 "张海凤,王玉珏,王劲璘,黄天佑,熊鹰(Cr ^{6*} 生物可利用度检测的微生物全细胞传感器 CBIO 的构建及其响应特征 侯启会,马安周,庄绪亮,庄国强(反硝化脱硫工艺中微生物群落结构及动态分析 "庆北院和市场大加市区",中海,在"大水",中海,是"大",中海,"大","大","大","大","大","大","大","大","大","大"	1204)
有序介孔碳载金/L-赖氨酸/纳米金修饰电极的制备及其对邻苯二酚、对苯二酚的检测响应研究	1211)
《环境科学》征订启事(942) 《环境科学》征稿简则(992) 信息(932,949,1061,1210) 专辑征稿通知(1173)

乙酸/丙酸作为 EBPR 碳源的动力学模型研究(II)——动力学模拟

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摘要:以乙酸和丙酸作为混合碳源,采用 2 组序批式反应器(SBR)研究聚磷菌(PAO)和聚糖菌(GAO)代谢过程中的物质转化规律. PAO 和 GAO 动力学模型共包含 7 个计量学参数和 24 个动力学参数. 根据计量学方程,推导了 PAO 和 GAO 动力学模型中的计量学参数. 结合试验结果,确定了动力学参数的取值. 采用 Matlab 软件积分计算了 PAO 和 GAO 胞内物质的变化规律. SBR 运行的实际值与模拟值相吻合,表明基于 SCFAs 代谢的动力学模型能够很好地模拟 PAO 和 GAO 的好氧/厌氧代谢过程.

关键词:聚磷菌;聚糖菌;计量学参数;动力学参数;动力学模拟中图分类号: X11 文献标识码: A 文章编号: 0250-3301(2013)03-0998-06

Kinetic Model of Enhanced Biological Phosphorus Removal with Mixed Acetic and Propionic Acids as Carbon Sources (II): Process Simulation

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Abstract: Two groups of sequencing batch reactors were used to study the metabolism substrate transformation of phosphorus-accumulating organisms (PAO) and glycogen-accumulating organisms (GAO) fed with mixed acetic and propionic acids. Seven stoichiometry parameters and 24 kinetic parameters were contained in the PAO and GAO kinetic model, and stoichiometry parameters were deduced from the stoichiometry models, while kinetic parameters were determined by experimental results. The kinetic model parameters of stoichiometry and kinetics were determined according the experiments and the literature. Subsequently, the substrate transformations of PAO and GAO were calculated by the Matlab software. The model curves matched the SBR experimental data well, indicating that the kinetic model based on SCFAs metabolism could be used to simulate PAO and GAO in anaerobic-aerobic conditions. Key words:phosphorus-accumulating organisms (PAO); glycogen-accumulating organisms (GAO); stoichiometry parameters; kinetic parameters; kinetic model

活性污泥模型的验证是新模型推出过程中必不可少的工作.模型验证分为实验室验证和现场验证,与现场验证相比,实验室验证获取的模型参数受外界干扰较小,而且由于物种纯度高,能够反映其真实代谢规律.课题组之前建立了基于 SCFAs 代谢的聚磷菌(PAO)和聚糖菌(GAO)动力学模型[1],为了确定模型参数、检验模型的可靠性,本研究采用序批式反应器(sequencing batch reactor, SBR)研究混合碳源对 PAO 和 GAO 代谢动力学的影响.

1 试验方法与试验结果

采用 2 组序批式反应器,包括 5 个 PAO-SBR 和 5 个 GAO-SBR. 每组反应器分别采用 5 个不同乙酸/丙酸比例(乙酸: 丙酸 为10:1、2:1、1:1、1:2、

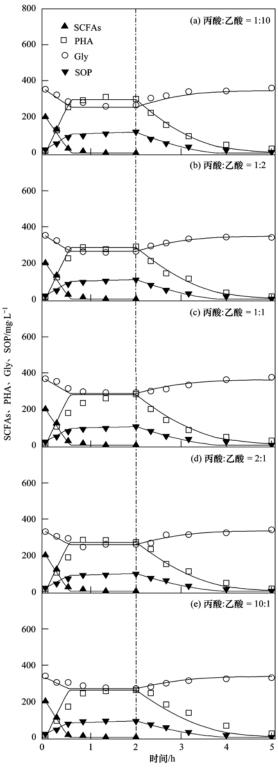
1:10) 对微生物进行长期驯化.每个 SBR 每个 SBR 反应器的有效容积 3.5 L,每天运行 3 个周期,每个周期 8 h,其中包括厌氧 2 h,好氧 3 h,沉淀 1 h,排水 5 min,静置 115 min.每个周期进水体积 2.75 L,厌氧 pH 为 6.8,进水时间 15 min.反应器好氧阶段溶解氧为 6 mg·L⁻¹左右以保证溶解氧不是好氧阶段的限制因素,污泥龄为 10 d 左右.在试验测定周期,采用手动瞬时进水,以便获取精确的周期数据.瞬时进水完毕后,每个 SBR 中混合有机酸总浓度为

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200 mg·L⁻¹, PAO-SBR 磷浓度为 20 mg·L⁻¹, GAO-SBR 磷浓度为 1.3 mg·L⁻¹, 然后每隔一段时间取样,测定系统中的 SCFAs、PHA、Gly、SOP 的变化情况(图 1、图 2 中的散点).



点代表测量值,线代表模拟值,下同

图 1 动力学模型模拟 PAO-SBR 物质转化规律

Fig. 1 Calibrated kinetic model describing the transformations in PAO-SBRs

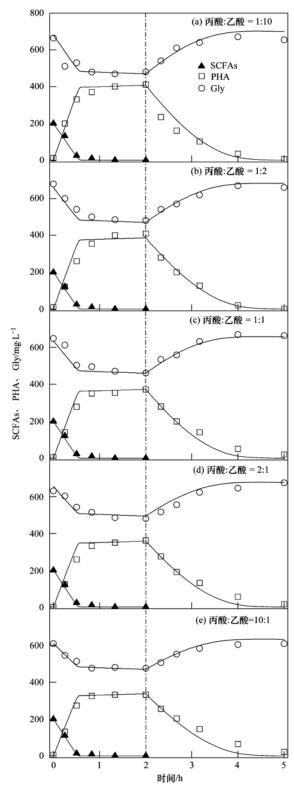


图 2 动力学模型模拟 GAO-SBR 物质转化规律

Fig. 2 Calibrated kinetic model describing the transformations in GAO-SBRs

2 模型参数的确定

2.1 计量学参数

聚羟基烷酸(poly-β-hydroxyalkanoates, PHA)

(1)

包括聚羟基丁酸 (poly-β-hydroxybutyrate, PHB)、聚羟基戊酸 (poly-β-hydroxyvalerate, PHV)、聚羟基2 甲基戊酸 (poly-β-hydroxy-2-methylvalerate, PH2MV),为了简化方程,本研究没有将这3 种物质单独列出. 需要指出,与以往的文献中 X_{PHA} 只包含 X_{PHB} 不同 $^{[2-5]}$,虽然本研究以 X_{PHA} 代替了

 X_{PHB} 、 X_{PHV} 和 X_{PH2MV} ,但是,通过设置比例系数 x,这里的 X_{PHA} 实质上为 X_{PHB} 、 X_{PHV} 和 X_{PH2MV} 三者之和,其中 x 为丙酸占总酸的 mol 比例(以 C 计)^[6].

式(1)为 PAO 代谢混合有机酸的厌氧计量学方程(各系数单位为 mol,以 C 或 P 计)^[6]:

$$-\operatorname{SCFAs} - \left(\frac{1}{2} - \frac{1}{6}x\right)\operatorname{Glycogen} - \left(\frac{1}{3} - \frac{1}{9}x + \alpha_{\text{PAO}}\right)\operatorname{HPO}_{3}(\operatorname{Poly-P}) + \frac{2\left[\frac{2}{3}(1-x)\right]^{2}}{\left(\frac{2}{3} - \frac{4}{9}x\right)}\operatorname{PHB} +$$

$$\left(\frac{5}{9}x + \frac{5\left[\frac{2}{3}(1-x)\right]\left(\frac{2}{9}x\right)}{\left(\frac{2}{3} - \frac{4}{9}x\right)}\right) PHV + \frac{3\left(\frac{2}{9}x\right)^{2}}{\left(\frac{2}{3} - \frac{4}{9}x\right)} PH2MV + \left(\frac{1}{3} - \frac{1}{9}x + \alpha_{PAO}\right) H_{3}PO_{4} + \left(\frac{1}{6} - \frac{1}{18}x\right) CO_{2} = 0$$

式中, α_{PAO} 为 1 mol 有机酸(以 C 计)通过 PAO 细胞膜所需的能量,当 pH 为中性时, α_{PAO} = 0. 11,这样由式(1)可以计算出 PAO 动力学模型中^[6]的 Y_{SOP}^{SCFAs} 、 Y_{PHA}^{SCFAs} 和 Y_{GLY}^{SCFAs} 分别为(以 COD 计):

$$Y_{\text{SOP}}^{\text{SCFAs}} = \frac{31(3 - x + 9\alpha_{\text{PAO}})}{16(18 + 3x)}$$
$$Y_{\text{PHA}}^{\text{SCFAs}} = \frac{9}{6 + x}$$
$$Y_{\text{GLY}}^{\text{SCFAs}} = \frac{3 - x}{6 + x}$$

当 0 ≤ x ≤ 1 时,上述参数可以简化为:

 $Y_{\text{SOP}}^{\text{SCFAs}} = \frac{31(3 - x + 9\alpha_{\text{PAO}})}{16(18 + 3x)}$ \$\approx 0.42 - 0.15x(g \cdot g^{-1})\$ (2)

$$Y_{\text{PHA}}^{\text{SCFAs}} = \frac{9}{6+x} \cong 1.50 - 0.21x(\text{g} \cdot \text{g}^{-1})$$
 (3)

$$Y_{\text{GLY}}^{\text{SCFAs}} = \frac{3-x}{6+x} \cong 0.50 - 0.21x(g \cdot g^{-1})$$
 (4)

同理,可以根据 GAO 的厌氧计量学方程^[6]以及 PAO 和 GAO 的好氧代谢计量学方程^[7],分别计算出 GAO 的厌氧的化学计量学常数以及 PAO 和 GAO 好氧计量学常数(表 1 和表 2).

表 1 过程计量学系数矩阵的参数值

Table 1 Matrix of the stoichiometric coefficients for metabolic model

		Table 1 M	latrix of the	stoichiometric coef	ficients for n	netabolic mo	del			
项目	参数		量比		质量比					
		乙酸	丙酸		乙酸	丙酸	混合酸			
	$Y_{ m SOP}^{ m SCFAs}$	0.43	0. 32	n(P)/n(C)	0.42	0. 27	0. 42 – 0. 15 <i>x</i>	m(P)/m(COD)		
厌氧 PAO	$Y_{ m PHA}^{ m SCFAs}$	1. 33	1. 22	n(C)/n(C)	1.50	1. 29	1.50 - 0.21x	m(COD)/m(COD)		
	$Y_{ m GLY}^{ m SCFAs}$	0.50	0. 33	n(C)/n(C)	0.50	0. 29	0.50 - 0.21x	m(COD)/m(COD)		
厌氧 GAO	$Y_{ m PHA}^{ m SCFAs}$	1. 75	1. 50	n(C)/n(C)	2. 00	1. 57	2. 00 - 0. 43 <i>x</i>	m(COD)/m(COD)		
八丰 GAO	$Y_{ m GLY}^{ m SCFAs}$	1.00	0.67	n(C)/n(C)	1.00	0.57	1. $00 - 0.43x$	m(COD)/m(COD)		
	$Y_{ m sx}^{ m max}$	0. 74	0. 80	n(C)/n(C)	0. 74	0. 73		m(COD)/m(COD)		
好氧 PAO ^[8,9]	$Y_{ m spp}^{ m max}$	3. 68	3. 34	n(P)/n(C)	3. 17	2.64		m(P)/m(COD)		
	$Y_{ m sgly}^{ m max}$	0.90	1.06	n(C)/n(C)	0.80	0.86		m(COD)/m(COD)		
	i_{PBM}^{-1}	0.015	0. 015	n(P)/n(C)	0.013	0.013	0. 013	m(P)/m(COD)		
	$Y_{\text{PAO}} = Y_{\text{sx}}^{\text{max}}$				0.74	0.73	0. 74	m(COD)/m(COD)		
关系	$Y_{\rm PHA} = 1/Y_{\rm sx}^{\rm max}$				0.32	0.38	0.32 + 0.06x	m(COD)/m(P)		
	$Y_{\rm GLY} = Y_{\rm sgly}^{\rm max}$				0.80	0.86	0.80 + 0.06x	m(COD)/m(COD)		
好氧 GAO ^[10, 11]	$Y_{\rm sx}^{\rm max}$ ($Y_{ m GAO}$)	0.75	0. 73	n(C)/n(C)	0. 74	0. 67	0.74 - 0.07x	m(COD)/m(COD)		
好利 GAU	$Y_{ m sgly}^{ m max}$ ($Y_{ m GLY}$)	0. 95	1. 04	n(C)/n(C)	0.83	0.85	0.83 + 0.02x	m(COD)/m(COD)		

¹⁾ PAO 和 GAO 的结构式^[12] 均可表示为 CH_{2.09} O_{0.54} N_{0.20} P_{0.015}

2.2 q_{GLY} 和 q_{PP} 的确定

在进行过程模拟之前,大多数的动力学参数选择为系统的默认值;但是部分动力学参数如 q_{SCFAs}

和 $m_{\text{GAO}}^{\text{Anaerobic}}$,根据课题组之前的研究^[6]进行计算,并与文献值进行了比较(表 2 和表 3).

2.3 其它模型参数的确定

表 2 本研究与文献中的过程计量学和动力学系数比较(pH 7.0)

Table 2 Comparison of the stoichimetric and the kinetic parameters in this study and the literature

∠ 161.	PAO GAO						W.D.					
参数	物理意义	[21,22]	[23]	[24]	[3]	[5]	本研究1)	[24]	[3]	[5]	本研究 ¹⁾	单位
计量学												
Y _{PHA} SCFAs2)	PHA 产率系数(PHA/SCFAs)	_	1.49	1.33	1.30	1.43	1.50 ~ 1.29	1. 33	2. 17	1.91	2.00 ~ 1.57	$[m(COD)/m(COD)]/g \cdot g^{-1}$
$Y_{\rm GLY}^{\rm SCFAs2}$	吸收 SCFAs 所消耗的糖原	_	0.49	0.33	0.30	0.43	0.50 ~ 0.29	0.33	1. 17	0.91	1.00 ~ 0.67	$[m(COD)/m(COD)]/g \cdot g^{-1}$
$Y_{\text{SOP}}^{\text{SCFAs2}}$	SOP 产率系数(SOP/SCFAs)	_	0.60	0.53	0.53	0.57	0.42 ~ 0.27	_	_	_	_	$[m(P)/m(COD)]/g \cdot g^{-1}$
$Y_{\text{PAO,GAO}}$	产率系数(生物量/PHA)	0.63	0.63	0.58	0.63	0.63	0.74	0.58	0.63	0.63	_	$[m(COD)/m(COD)]/g \cdot g^{-1}$
Y_{PHA}	贮存聚磷所需要的 PHA	0. 20	0.20	0.32	0.20	0.20	0.32 ~ 0.38	_	_	_	0.74 ~ 0.67	$[m(COD)/m(P)]/g \cdot g^{-1}$
$Y_{\rm GLY}$	糖原产率系数(GLY/PHA)	_	_	1.00	1.00	1.00	0.80 ~ 0.86	1.00	1.00	1.00	0.83 ~ 0.85	$[m(COD)/m(COD)]/g \cdot g^{-1}$
PBM	微生物中的磷含量	0.02	_	_	_	0.02	0.013	0.02	_	_	0.013	$[m(P)/m(COD)]/g \cdot g^{-1}$
动力学												
I _{SCFA} 3)	SCFAs 吸收速率常数			0. 19 ~ 0. 2	l		0. 19 ~ 0. 21		0. 205		0. 205	$[m(\text{COD})/m(\text{COD}) \cdot t]/g \cdot (g \cdot d)^{-1}$
l _{GLY} ⁴⁾	GLY 的水解速率常数	_	3	3.8	2. 7	2. 25	2. 32 ~ 1. 69	1.2	2. 7	3	4. 32 ~ 2. 88	$[m(\text{COD})/m(\text{COD}) \cdot t]/g \cdot (g \cdot d)^{-1}$
(PP 4)	PP 的水解速率常数	1.5	1.5	2.8	2	1.5	1. 52 ~ 1. 09	_	_	_	_	$[m(P)/m(COD) \cdot t]/g \cdot (g \cdot d)^{-1}$
mAnaerobic PAO, GAO	PAO,GAO 厌氧维持系数	_	_	_	_	_	0.07	_	_	_	0.11	d -1
L _{PAO} , GAO	最大生长速率	1	1	0.84	1	0.7	0.8	0.8	1	0.7	0.6	d -1
	$X_{\text{PAO, GAO}}$ 的溶菌速率常数	0.2	0.15	0.08	0.2	0.15	0. 1	0.08	0.1	0. 15	0.1	d -1
b_{PP}	X_{PP} 的分解速率常数	0.2	0.07	0.08	0.2	0.07	0. 1	_	_	_	_	d -1
$b_{ m GLY}$	X_{GLY} 的分解速率常数	0.2	0.2	0.08	0.2	0.2	0. 1	0.08	0.1	0.2	0.1	d -1
$b_{ m PHA}$	X_{PHA} 的分解速率常数	0.2	0.2	0.08	0.2	0.2	0. 1	0.08	0.1	0.2	0.1	d -1
$K_{\rm SCFAs}$	$S_{ m SCFAs}$ 的饱和系数	4	4	3.63	4	4	3.6	3.63	4	4	3.6	$[m(P)/V]/g \cdot m^{-3}$
$K_{\rm GLY}$	X_{GLY} 的饱和系数	_	0.01	0.001	0.001	0.01	0.001	0.001	0.001	0.01	0.001	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K_{O2}	O_2 的饱和常数	0.2	_	0.2	_	_	0. 2	0.2	_	_	0.2	$[m(O_2)/V]/g \cdot m^{-3}$
X_{PP}	X_{PP} 的饱和系数	0.01	0.02	0.01	0.01	0.01	0.001	_	_	_	_	$[m(P)/m(COD)]/g \cdot g^{-1}$
K_{PS}	PP 贮存的磷的饱和系数	0.2	0.2	0.2	0.5	0.1	0.5	_	_	_	_	$[m(P)/V]/g \cdot m^{-3}$
$K_{\mathbf{P}}$	生长过程磷的饱和系数	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	$[m(P)/V]/g \cdot m^{-3}$
Max PP	X_{PP}/X_{PAO} 的最大比率	0.34	0.34	0.28	0.34	0.4	0.35	_	_	_	_	$[m(P)/m(COD)]/g \cdot g^{-1}$
f Max GLY	$X_{\rm GLY}/X_{\rm PAO}$ 或 $X_{\rm GLY}/X_{\rm GAO}$ 的最大比	率 —	0.4	0. 25	0. 15	0.2	0. 2	0.4	0.3	0.425	0.425	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K_{IPP}	X _{PP} 贮存的抑制系数	0.02	0.02	0.001	0.02	0.001	0.001	_	_	_	_	$[m(P)/m(COD)]/g \cdot g^{-1}$
K_{IG}	X_{GLY} 贮存的抑制系数	0.02	_	0.015	0.02	0.02	0.02	0.015	0.02	0.02	0.02	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K _{PHA-PP}	用于 X_{PP} 贮存的 PHA 饱和系数	0.01	0.02	0.07	0.05	0.05	0.04	_	_	_	_	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K_{PHA}	用于生长的 PHA 饱和系数	_	0.02	0.03	0.05	0.025	0.015	0.03	0.01	0.02	0.01	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K _{PHA-GLY}	用于 X_{GLY} 贮存的 PHA 饱和系数	0.01	0.02	0.12	0.01	0.05	0. 1	0.008	0.01	0.01	0.1	$[m(COD)/m(COD)]/g \cdot g^{-1}$
K _{pH} ⁵⁾	H +浓度的饱和常数			2. 28 × 10 ⁻	6		2. 28×10^{-6}	_	_	_	_	$[n(H^+)/V]/\text{mol}\cdot\text{m}^{-3}$
K _{I,pH} ⁵⁾	H +浓度的抑制常数			6. 94 × 10 ⁻			6. 94×10^{-4}	_	_	_	_	$[n(H^+)/V]/\text{mol}\cdot\text{m}^{-3}$

1)本栏的计量学参数与 SCFAs 酸的类型及比例有关 $^{[6]}$; 2)原文献中没有直接列出,但是根据参数的物理意义可以计算出计量学系数,参数转换关系如下; $Y_{\rm PHA}^{\rm SCFAs}=1/Y_{\rm SA}$, $Y_{\rm SCA}^{\rm SCFAs}=(1-Y_{\rm SA})/Y_{\rm SA}$, $Y_{\rm SOP}^{\rm SCFAs}=Y_{\rm SOP}/Y_{\rm SA}$; 3)见文献 [10,12,14,16,25]; 4)见表 3; 5)见文献 [26,27]

表 3 动力学参数 q_{GLY} 、 q_{PP} 的选择 $^{1)}$

Table 3 Determination of $q_{\rm GLY}$ and $q_{\rm PP}$

项目		乙酸		丙酸				
火日	文献	$q_{ m GLY}$	$q_{ m PP}$	文献	$q_{ m GLY}$	q_{PP}		
	Smolders 等 ^[13]	0.0627	0. 040 1	Oehmen 等 ^[14]	0. 015 4	0. 022		
	Pijuan 等 ^[15] 的试验数据	0.027	_	Pijuan 等 ^[15] 的试验数据	0.021	_		
	Pijuan 等 ^[15] 的模型数据	0. 17	0. 208	Pijuan 等 ^[15] 的模型数据	0. 15	0. 208		
PAO	Oehmen 等 ^[16]	0.0264	_	Oehmen 等 ^[16]	0.0209	_		
	Lu 等 ^[17]	0. 053 5	0.0376	Lu 等 ^[17]	0. 038 3	0. 028 7		
	Filipe 等 ^[18]	0.04	0.1	Oehmen 等 ^[9]	0.0263	0. 022 9		
	本研究	0. 0964	0.0633	本研究	0.0704	0. 045 3		
	Filipe 等 ^[19]	0. 191 5	_			_		
GAO	Zeng 等 ^[11]	0.068	_	Zeng 等 ^[11]	0. 041 1	_		
GAU	Oehmen 等 ^[16,20]	0. 081 4	_	Oehmen 等 ^[16,20]	0.0402	_		
	本研究	0.18		本研究	0. 12			

¹⁾部分文献没有直接给出具体的试验数据,该表是根据文献中数据计算而得; q_{GLY} :[$m(\text{COD})/m(\text{COD}) \cdot t$]/g·(g·h) $^{-1}$; q_{PP} :[$m(\text{COD})/m(\text{COD}) \cdot t$]/g·(g·h) $^{-1}$

其它模型参数的选择见表3,这些参数主要选 自活性污泥 ASM2 模型中的推荐值[21,22]. 除少数 几个参数之外,模型中所使用的大多数计量学和动 力学数据都与文献中数据保持一致. 少数参数与 ASM2 模型不一致的主要原因是:①本研究的碳源 中包含一部分丙酸,而使用 ASM2 模型的文献中基 本是以乙酸作为唯一碳源;②在厌氧阶段,文献以 PHA 的合成作为厌氧动力学的基准方程,而本研究 以 SCFAs 的代谢作为厌氧动力学的基准方程: ③表 2 中一般采用 $\mu_{PAO} = \mu_{GAO}$,而本研究中 $\mu_{PAO} > \mu_{GAO}$, 这是因为,根据文献报道,每吸收1 mol(以C计)乙 酸或丙酸,将在好氧条件下合成 0.32 ~ 0.37 mol PAO或 GAO(以 C 计),换言之,代谢相同量的有机 酸时,生成的微生物的量也相同[10]. 如果本研究也 采用 $\mu_{PAO} = \mu_{GAO}$,则合成的 GAO 约为 PAO 的 1.33 倍,与文献不符,因此,本研究中 μ_{PAO} = 1.33 μ_{GAO} .

3 数据模拟与验证

将表 1~3中的计量学和动力学数据代入到动力学矩阵及过程速率中,采用 Matlab 软件进行积分,即可绘出混合酸条件下 PAO 和 GAO 的厌氧-好氧过程中物质变化曲线(图 1、图 2). 由图 1、图 2可见,模拟曲线和试验数据比较相符,这说明使用以SCFAs 作为基准物质的 PAO(和 GAO)厌氧和好氧动力学模型、并赋予相应的计量学和动力学参数可以很好地模拟有机酸、糖原、PHA 和 SOP 的变化规律.

4 结论

- (1)采用 10 个 SBR 反应器,分别测定了 PAO和 GAO 在厌氧和好氧条件下 SCFAs、PHA、Gly、SOP 的变化情况.
- (2)确定了 PAO 和 GAO 动力学模型中的计量学参数和动力学参数的取值范围,特别是几个关键参数如 $Y_{\text{SOP}}^{\text{SCFAs}}$ 、 $Y_{\text{PHA}}^{\text{SCFAs}}$ 、 $Y_{\text{GLY}}^{\text{SCFAs}}$ 、 q_{GLY} 和 q_{PP} 的选取和计算过程,在不同进水碳源组成条件下,部分参数值的选取会有所变化.
- (3) Matlab 的积分结果表明,基于 SCFAs 代谢 建立的动力学模型能够较好地模拟 PAO 和 GAO 的 代谢过程,因此,该模型可以用来预测不同碳源条件 下 PAO 和 GAO 的竞争规律.

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HUANJING KEXUE

Environmental Science (monthly)

Vol. 34 No. 3 Mar. 15, 2013

CONTENTS

Estimation of DM Estimated the MODIS Association of David University David Description of New Johnson	CHO I:
Estimation of PM _{2,5} over Eastern China from MODIS Aerosol Optical Depth Using the Back Propagation Neural Network Comparison of Atmospheric Particulate Matter and Aerosol Optical Depth in Beijing City	
Impacts of Meteorological Factors on Atmospheric Methane Mole Fractions in the Background Area of Yangtze River Delta	PU Jing-Jiao, AU riong-nui, GU Jun-qiang, et al. (853)
Dispersion and Analysis of Odor Pollution in Landfill Area Under the Enclosed Operation Condition	
Distribution Characteristics and Sea-Air Fluxes of Volatile Halocarbons in the East China Sea in Winter	
Intra- and Inter-annual Variabilities of Particulate Organic Matter in the Mirs Bay from 2000 to 2010	
Phytoplankton Assemblages and Their Relation to Environmental Factors by Multivariate Statistic Analysis in Bohai Bay	······ ZHOU Ran, PENG Shi-tao, QIN Xue-bo, et al. (864)
Characteristics and Evolution of Hydrochemical Compositions of Freshwater Lake in Tibetan Plateau	· · WANG Peng, SHANG Ying-nan, SHEN Li-cheng, et al. (874)
Estimation of Nonpoint Source Pollutant Loads and Optimization of the Best Management Practices (BMPs) in the Zhangweinan Rive	er Basin XU Hua-shan, XU Zong-xue, LIU Pin (882)
An Object-Oriented Intelligent Engineering Design Approach for Lake Pollution Control	ZOU Rui ZHOU Jing LIU Yong et al. (892)
Contribution of Plant Litters to Sediments Organic Matter in Jiulong River Estuary Wetland	
Application of Tiered Approach to Assess the Impact of Backfilling Remediated Soil on Groundwater	
Removal of Nitrate from Groundwater Using Permeable Reactive Barrier	II Vin li VANC lun iun III Vino vin et al. (014)
Research on Pollution Load of Sediments in Storm Sewer in Beijing District	LI Alu-II, TANG Juli-Juli, LO Alao-xia, et al. (214)
• 0	
Occurrence and Risk Assessment of Five Selected PPCPs in Municipal Wastewater Treatment Plant and the Receiving Water	WEN Zhi-hao, DUAN Yan-ping, MENG Xiang-zhou, et al. (927)
Microbial Risk Assessment of Urban Water Bodies for Aesthetical and Recreational Uses	
Study on Removal of Di-(2-Ethylhexyl) Phthalate by Using of Small-Scale Biological Aerated Filter	
Mechanism of Membrane Fouling and Filtration Characteristics in a Membrane Bioreactor for Industrial Wastewater Treatment	
Enhanced Electro-Chemical Oxidation of Acid Red 3R Solution with Phosphotungstic Acid Supported on γ-Al ₂ O ₃ ····································	········· YUE Lin, WANG Kai-hong, GUO Jian-bo, et al. (955)
Degradation Kinetics of Activated Carbon Catalyzed Persulfate Oxidation Orange G	·········· YANG Mei-mei, ZHOU Shao-qi, LIU Dan, et al. (962)
Study on the Start-up of the Anaerobic Baffled Reactor for Treating Alkali-deweighting and Dyeing-printing Wastewater	
Study on the Pollutants Removal Performance Along the Advanced Treatment in Tannery Wastewater by O ₃ -BAF	······································
Effect of Pilot UASB-SFSBR-MAP Process for the Large Scale Swine Wastewater Treatment	·· WANG Liang CHEN Chong-jun CHEN Ying-yu et al. (979)
Cultivation of Aerobic Granular Sludge with Municipal Wastewater and Studies on Its Characteristics Under the Continuous Flow	
Kinetic Model of Enhanced Biological Phosphorus Removal with Mixed Acetic and Propionic Acids as Carbon Sources (I): Model	
Kinetic Model of Enhanced Biological Phosphorus Removal with Mixed Acetic and Propionic Acids as Carbon Sources (II): Process	
Kinetic Model of Enhanced Biological Phosphorus Removal with Mixed Acetic and Propionic Acids as Carbon Sources (III): Model	
Comparative Study on Water-air CO2, CH4 Flux in Two Tributaries in the Three Gorges Reservoir, China	
Factors Influencing the Spatial Variability in Soil Respiration Under Different Land Use Regimes	····· CHEN Shu-tao, LIU Qiao-hui, HU Zheng-hua, et al. (1017)
Differences in Soil Respiration Between Cropland and Grassland Ecosystems and Factors Influencing Soil Respiration on the Loess Pl	ateau ·····
	· ZHOU Xiao-gang, ZHANG Yan-jun, NAN Ya-fang, et al. (1026)
Application and Benefit Evaluation of Tiered Health Risk Assessment Approach on Site Contaminated by Benzene	
History of Heavy Metal Pollution from Tidal Flat in Haizhou Bay	ZHANG Rui ZHANG Fan LIII Fu-cheng et al. (1044)
Accumulation, Distribution and Pollution Assessment of Heavy Metals in Surface Sediment of Caohai Plateau Wetland, Guizhou Pro	
Accumulation, Distribution and Foliation Assessment of Heavy steals in Surface Seament of Gaonal Flateau Wetania, Outziou 110	7HANC Oing hai LIN Chang hu TAN Hang at al. (1055)
Assessment and Correlation Analysis of Heavy Metals Pollution in Soil of Dajinshan Island	CHENC Forg CHENC lin ping SANC Hong obun et al. (1062)
Fraction Distribution and Risk Assessment of Heavy Metals in Stream Sediments from a Typical Nonferrous Metals Mining City	
Contamination and Health Risk for Heavy Metals via Consumption of Vegetables Grown in Fragmentary Vegetable Plots from a Typic	al Nonferrous Metals Mine City
	····· LI Ru-zhong, PAN Cheng-rong, XU Jing-jing, et al. (1076)
Correlativity Study of the Distribution of Soil Magnetic Susceptibility and the Heavy Metal Contents in Xi'an City	
Distribution Characteristics and Environmental Significance of Heavy Metals in Soil Particle Size Fractions from Tropical Forests in C	lhina ·····
Domination of the Control of the Con	
Study on Phosphorus Adsorption Characteristic of Sediments in an Ecological Ditch	···· ZHANG Shu-nan, JIA Zhao-yue, XIAO Run-lin, et al. (1101)
Fractions and Adsorption Characteristics of Phosphorus on Sediments and Soils in Water Level Fluctuating Zone of the Pengxi River,	a Tributary of the Three Gorges Reservoir
	SUN Wen-bin DU Bin ZHAO Xiu-lan et al. (1107)
Sorption Behavior of Triton X-100 on Loess and Affecting Factors	
Residual Levels in Air, Soil and Soil-Air Exchange of Organochlorine Pesticides in Hami Region of Xinjiang and Its Potential Ecolog	
residual Levels in Air, 30ir and 30ir Air Exchange of Organochiothic Festicides in Haim Region of Airijiang and its Foreitial Leono	MA 7: long MAO Vice much DINC 7hong much et al. (1120)
Levels and Sources of Decabromodiphenyl Ether and Dechlorane Plus in Xining and Tianjun, Qinghai Province, China	
Vertical Distribution of PBDEs and DL-PCBs in Sediments of Taihu Lake	
Characteristics of Organic Pollutants in the Sediments from a Typical Electronics Industrial Zone	
Emission Characteristics of Polycyclic Aromatic Hydrocarbons in Exhaust Particles from a Diesel Car	
Characterization of PAHs in Fly Ashes from Coke Production · · · · · · · · · · · · · · · · · · ·	
Comparison of PAHs Distribution in Stabilized Sludge by Sludge Drying Bed and Reed Bed	······ CUI Yu-bo, SUN Hong-jie, RAN Chun-qiu, et al. (1161)
Effects of Adsorbents on Partitioning and Fixation of Heavy Metals in the Incineration Process of Sewage Sludge	LIU Jing-yong, SUN Shui-yu, CHEN Tao (1166)
Environmental Toxicity of Waste Foundry Sand	
Construction and Properties of a Microbial Whole-cell Sensor CB10 for the Bioavailability Detection of Cr ⁶⁺	
Structure and Dynamics of Microbial Community in the Denitrifying Sulfide Removal Process	
Effects of Physico-chemical Parameters on the Abundance of the Denitrification-associated Genes nirK, nirS and nosZ During Agricu	
Effects of Physico-chemical Parameters on the Abundance of the Denitrification-associated Genes nith, nits and nosz During Agricu	HII Chan vice CHEN Version THANG P. 1 / (1100)
Impact of PAHs on the Expression of PRDX in Earthworm (Eisenia fetida)	
Preparation of OMC-Au/L-Lysine/Au Modified Glassy Carbon Electrode and the Study on Its Detection Response to Hydroquinone at	nd Catechol
Topaution of State 1 and	ZHOU Yao-vu TANG Lin LI Zhen et al. (1211)
Risk Communication in Construction of New Nuclear Power Plant	

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