

SBR 生物技术处理竹浆造纸黑液的研究*

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摘要 通过循序间歇式活性污泥法(SBR)处理可使经酸析木质素后所得黑液中的 BOD_5 和 COD 显著减少, 当进水中 COD 浓度为 $1090\text{--}1170\text{mg/L}$ 时, BOD_5 去除率为 $70\%\text{--}83\%$, COD 去除率为 $54.5\%\text{--}63\%$, 出水中 BOD_5 和 COD 的浓度分别为 $76\text{--}101\text{mg/L}$ 和 $419\text{--}500\text{mg/L}$. 内电解与 SBR 联合对黑液的处理更为有效. 当进水 COD 浓度为 $1046\text{--}1100\text{mg/L}$ 时, BOD_5 和 COD 去除率分别为 $67\%\text{--}68\%$ 和 $71.4\text{--}76.9\%$, 出水 BOD_5 和 COD 浓度分别达 $33\text{--}48\text{mg/L}$ 和 $242\text{--}315\text{mg/L}$, 符合 GB 8978-88 国家排放标准. 内电解显著提高了后续 SBR 处理的效果. 研究了 COD 一级降解反应动力学, 得到了动力学常数 K_1 和不可生化降解的 COD 浓度. 模拟数据与试验数据吻合良好.

关键词 SBR 生物技术, 内电解, 竹浆, 黑液, 生物降解, COD_{Cr} , BOD_5 , COD 降解动力学.

造纸黑液是环境污染的主要污染源之一, 而蒸煮黑液的污染又占其总污染负荷的 90% 以上^[1]. 本文通过采用内电解-循序间歇式活性污泥法(Sequencing Batch Reactor, SBR)处理竹浆造纸黑液的研究, 探讨该种废水的有效治理途径.

1 试验材料与方法

1.1 废水来源与水质

废水取自广东某硫酸盐法竹浆造纸厂. 经分析, 前后3批水样的水质列于表1(均为多次分析的平均值).

表1 黑液水质状况/ $\text{mg}\cdot\text{L}^{-1}$

水样	pH	COD_{Cr}	BOD_5	木质素
1	10—11	2600	707	2824
2	10—11	3500	435	3723
3	10—11	8750	1090	6010

1.2 试验装置

(1) SBR 该装置见图1. 反应器用有机玻璃制成, 总容积 60L , 有效容积 48L , 反应器底部设置微孔曝气器, 用空压机供气. 反应器上设置了多个排水口, 可根据需要排出不同分量的经处理并澄清后的上清液, 下部设置排泥口. 进水、出水速度用恒流泵控制. 进水、曝气、沉淀、排水、静置等运行程序用程序控制器自动控制.

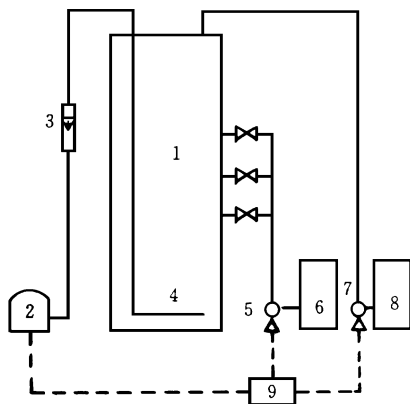


图1 SBR 装置示意图

1. 反应器 2. 空压机 3. 转子流量计
4. 微孔曝气器 5. 排水泵 6. 出水箱
7. 进水泵 8. 配水箱 9. 自动控制装置

(2) 内电解装置 内电解装置见图2. 柱内按一定比例装满废铁屑和石墨, 充填率约 80% , 柱底部装有布水板、进水管和截止阀, 柱上部有出水管. 另外为增强氧化能力, 在柱底部设有一充氧器.

1.3 分析方法

COD_{Cr} 、 BOD_5 采用标准方法^[2]. 木质素含量采用 751G 分光光度计测定, 具体方法参见参考

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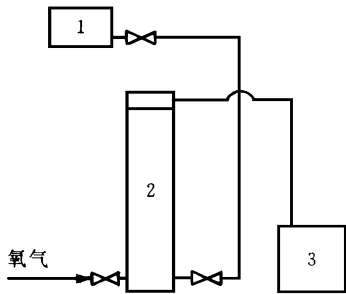


图2 内电解试验装置示意图

1. 高位槽 2. 内电解柱 3. 排水槽

1.4 工艺试验

工艺 I: 将造纸黑液中和至 pH3—3.5(反应温度60—65℃, 时间30min), 酸析木质素后的澄清液, 送至 SBR 系统处理.

工艺 II: 将造纸黑液中和至 pH3—3.5(反应温度60—65℃, 时间30min), 酸析木质素后的澄清液, 送至内电解进行预处理, 后将内电解排出液中中和至 pH7—8, 澄清后送至 SBR 系统处理.

1.5 活性污泥的培养与驯化

取城市综合污水处理厂新鲜活性污泥作为菌种, 按逐步增加酸析木质素后黑液(pH 调至7左右) 比例的办法, 对污泥进行同步培养和驯化. 用尿素作为氮源, 用 KH_2PO_4 作为磷源, 使培养液成分大致维持 $\text{BOD}_5 \cdot \text{N} \cdot \text{P} = 100 \cdot 5 \cdot 1$. 10d 后, 满负荷运行. 经2周培养后, 污泥沉降比达20%, 污泥浓度 (MLSS) 3000mg/L, BOD_5 去除率达80%以上. 经镜检, 可看到大量菌胶团, 并有相当量的游泳型纤毛虫(如草履虫) 及固着型纤毛虫(如等枝虫和盾纤虫), 也有少量轮虫. 至此培养和驯化期结束, 进入稳定运行阶段. 当废水性质发生变化时, 都安排一周驯化期, 以使操作条件和处理效果更趋稳定.

2 结果与讨论

2.1 酸析-SBR 工艺处理效果

对表1所列1和2号水样, 通过酸析除去大部分木质素后, 其黑液用 SBR 工艺进行处理, 酸析过程及 SBR 工艺的试验结果列于表2和表3.

表2 酸析前后黑液成分的变化¹⁾/ $\text{mg} \cdot \text{L}^{-1}$

水样	COD _{Cr}			BOD ₅			木质素		
	酸析前	酸析后	去除率/ %	酸析前	酸析后	去除率/ %	酸析前	酸析后	去除率/ %
1	2600	1115	57.1	707	498	29.6	2824	584.8	79.29
2	3500	1137.5	67.5	435	314.6	27.7	3723	705.9	81.0

1) 中和 pH3.0—3.5, 温度60—65℃, 反应时间30min, 沉降1h 之后的上清液为 SBR 工艺进水

表3 SBR 工艺的处理效果¹⁾/ $\text{mg} \cdot \text{L}^{-1}$

试验号	COD _{Cr}			BOD ₅			木质素		
	进水	出水	去除率/ %	进水	出水	去除率/ %	进水	出水	去除率/ %
1	1130	419	62.9	470	77	83.6	600	504	16
2	1100	500	54.5	526	101	80.8	569.6	495.5	13
3	1155.4	447.3	61.2	340.8	76.5	77.6	692.8	621.7	18.2
4	1088.5	470.1	56.8	314.5	87	72.3	725	634	12.5
5	1168.6	485.8	58.4	288.6	86.6	70.0	700	613.9	12.3

1) 操作程序: 进水2h, 曝气8h, 沉淀1h, 排水1h, 未静置; 试验号1和2采用废水样1, 试验号3—5采用废水样2; 每周期废水投配量为50%; MLSS 3000—3500mg/L

表2表明, 通过酸析, 黑液中 COD_{Cr}、BOD₅ 和木质素的去除率可分别达到57%—68%、28%—30%和79%—81%. 表3表明, 木质素去

除率很低, 说明它难被生物降解. 由于木质素衍生物是导致黑液 COD 和色度形成的主要原因, 所以 SBR 系统中 COD 去除率不高. 试验中

采用了2种水样,其BOD₅/COD比值有所不同,但进水COD浓度接近,出水COD浓度亦接近,均在400mg/L以上.黑液中的BOD₅主要为纤维素及半纤维素的降解产物,属于多糖类物质,降解性能好,故去除率较高.

2.2 酸析-内电解-SBR 工艺处理效果

本试验中SBR 操作程序与2.1相同,试验操作条件与2.1基本相同,但酸析木质素后的黑液先经内电解预处理,再进行SBR 生物处理,

表5 SBR 工艺(酸析-内电解后)处理效果¹⁾/mg·L⁻¹

试验号	COD _{Cr}			BOD ₅			木质素		
	进水	出水	去除率/%	进水	出水	去除率/%	进水	出水	去除率/%
1	1100.6	315.0	71.4	147.7	47.7	67.7			
2	1046.0	242.1	76.9	133.0	33.1	75.1	355.4	341.5	3.9
3	1070	246.7	76.9	139	45.1	67.2	600	347.7	4.2

1) 操作程序见表3注,使用水样3

2种工艺试验结果的比较表明,酸析木质素后的黑液经内电解预处理后,能够显著提高黑液中COD的去除率,平均从58.8%提高到75.1%,出水质量已达到GB8978-88国家排放标准.后1种工艺BOD₅去除率反较前1种工艺有所下降,这可能是由于内电解去除了相当部分的BOD₅,而COD的去除量相对较少,但其结构却发生了改变,而更有利于后续SBR 工艺对COD的去除.

2.3 SBR 系统中污泥沉降性能

SBR 系统控制MLSS 在3000—3500mg/L 范围内,从而SV₃₀.变化于18%—22%,SVI 维持在58%—65%,污泥沉降性能良好,菌胶团中未发现有丝状菌.SBR 起始反应和结束反应之间基质浓度及好氧与缺氧条件的交替变化,有效地抑制了丝状菌的生长,是SBR 活性污泥不易膨胀的原因.又因SBR 的沉降过程是在静止状况下进行,出水悬浮物浓度均在40mg/L 以下.

2.4 COD 降解的动力学分析

根据埃肯费尔德(Eckenfelder)等人所持的二相说,当基质浓度较低时,基质降解速度被残存的基质左右,与其浓度呈一级反应.试验中活性污泥浓度较高,且浓度相当稳定时,米-门

酸析-内电解及SBR 工艺试验结果分别列于表4和表5.

表4 酸析-内电解预处理效果/mg·L⁻¹

项目	酸析前	内电解进水 (酸析后)	内电解 出水	调pH至7后
COD _{Cr}	8750	3594	1294	1046
BOD ₅	1090	809.6	341.7	133.2
木质素	6010	1231.8	904.6	355.8

公式可简化为:

- dL_t/dt = K₁L_t (1)

式中,L_t为t时刻可降解溶解性COD浓度(mg/L);t为曝气时间(h);K₁为COD降解速度常数(h⁻¹).

设L₀为t= 0时进水后混合液中可降解溶解性COD浓度(mg/L),则方程(1)的解为:

L_t = L₀ × 10^{-K₁t} (2)

式中,K₁= K₁/2.3

试验中在起始时刻(t= 0)和任意t时刻所测得的COD浓度值用L₀和L_t表示,均指总的溶解性COD浓度值,包括可降解性和不可降解性2部分.设不可降解性的COD浓度值为L_∞,经t时间曝气后去除的COD浓度值为L_∞,下面2关系式显然同时成立:

L_∞ = L₀ - L_t (3)

L_∞ = L₀ - L_t (4)

式(2)代入式(4)得

L_∞ = L₀(1 - 10^{-K₁t}) (5)

通过式(5),从已知的一组(t,L_∞)值借托马斯图解法^[4]可求得K₁和L₀,L₀实质上表征着该种

废水的 COD 可最大处理程度;继而可从 L_0' 与 L_0 的差值求得废水中不可生化降解的 COD 浓度值 L_n ; $L_t = L_0' - L_n$ 求得 t 时刻混合液中可降解溶解性 COD 浓度值.

COD 降解过程如图3. 图3中曲线1—3对应于工艺 I, 试验原液未经内电解处理; 曲线4—6对应于工艺 II, 试验原液已经内电解处理. 图3表明, 内电解处理的原液经2h 曝气, COD 浓度就已降至350mg/L 以下, 未经内电解预处理的原液经8h 曝气, COD 浓度仍在450mg/L 以上, 曝气4h 以后, COD 降解过程均趋于平缓.

根据图3的数据经托马斯法处理和一元线性回归得 COD 降解动力学常数及相关参数 (表6). 一元线性回归相关系数均在0.988以上, 线性拟合良好. 说明 COD 降解过程较严格地遵循一级反应动力学规律. 酸析木质素后的

蒸煮黑液经内电解预处理, 使 COD 降解速度常数平均由 0.227h^{-1} 升至 0.268h^{-1} , 不可生化降解的 COD 浓度平均由427mg/L 降至197mg/L, 为进水 COD 浓度的21.5%.

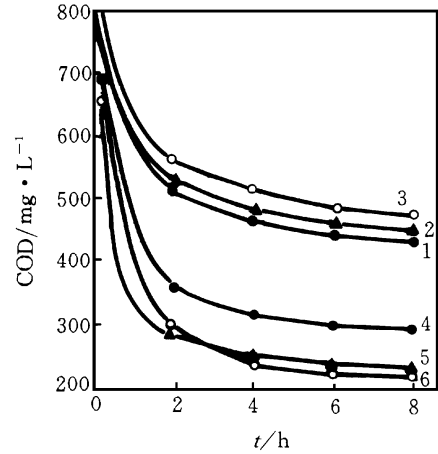


图3 COD 降解过程曲线

表6 COD 降解速度常数及相关参数

组号	K_1/h^{-1}	$L_0/\text{mg}\cdot\text{L}^{-1}$	$L_n/\text{mg}\cdot\text{L}^{-1}$	$L_t/t=8$	r
1	0.230	397.0	404.0	43.3	0.992
2	0.234	350.0	429.3	40.8	0.997
3	0.217	380.0	447.2	38.6	0.992
4	0.267	459.5	245.3	69.7	0.995
5	0.269	473.5	173.6	68.4	0.988
6	0.268	487.7	172.1	74.6	0.999

3 结论

(1) 制浆蒸煮黑液经酸析木质素后, 直接通过 SBR 系统处理可使 COD 去除率达54.5%—63%, BOD 去除率达70%—84%; 酸析木质素后的黑液经内电解预处理后再经 SBR 系统处理可使 COD 去除率达71%—77%, BOD 去除率达67%—75%. 后1种工艺的出水浓度达 GB 8978-88国家排放标准.

(2) COD 降解过程动力学分析表明, 其降解速率与可降解溶解性 COD 浓度之间严格遵循线性关系, 并由此可求出 COD 降解动力学常数和有关参数, 借此能判断废水最大可生化降解程度.

(3) 内电解与 SBR 联合处理技术对黑液的处理比单纯用 SBR 工艺处理更为有效. 内电解能够显著降低不可生化降解的 COD 浓度, 提高 COD 降解速率常数, 从而更有利于后续 SBR 工艺的处理.

参 考 文 献

1 戴友芝. 环境科学与技术, 1995, 1: 40
2 国家环保局. 水和废水监测分析方法. 北京: 中国环境科学出版社, 1989: 354—356, 362
3 [日]中野 三著, 高洁译. 木质素化学. 北京: 轻工业出版社, 1988: 219
4 R·S·拉马尔奥. 废水处理概论. 北京: 中国建筑工业出版社, 1982: 56—59

leached for ten years are more than 7, except the brown earth which become acid under pH 2 in the fourth year. The total losses of the leached base ions are: After ten years leaching, lime concretion black soil > salt-affected soil > chao soil > brown earth. The sensitivity of base ions to acid rain are: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+, \text{Na}^+$. The simulated acid rain has activation to the aluminium in the soils. There is no active aluminium in the four types of soils except the brown earth which the active aluminium appears in pH2. It has obvious improvement effect to apply lime to the acid brown earth.

Key words: simulated acid rain, simulated earth volume test, physical and chemical properties of soil, active aluminium.

A Study on the Treatment of Black Liquor from Bamboo Pulping Process with Sequencing Batch Reactor Biological Technique. Yan Shanguhua, Chen Min et al. (Guangdong University of Technology, Guangzhou 510090): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 30_33

In this paper, the treatment of bamboo pulping black liquor in which lignin has been separated by acid with sequencing batch reactor (SBR) was investigated. The experimental results showed that BOD₅ and COD in black liquor increased remarkably with the treatment of SBR, BOD₅ removal rate is 70%—83%, COD removal rate is 54.5%—63%, the effluent BOD₅ and COD after the treatment are 76—101 mg/L and 419—500mg/L respectively when influent COD is 1090—1170mg/L. The technology of combining internal decomposition with SBR is more efficient for treatment of black liquor, BOD₅ and COD removal rate are 67%—68% and 71.4%—76.9% respectively, the effluent BOD₅ and COD from this system are 33—48mg/L and 242—315mg/L respectively when influent COD is 1046—1100mg/L. It is in keeping with GB8978-88 effluent standard. The internal decomposition remarkably increase the effectiveness of follow-up SBR treatment. In addition, the kinetics of first order degradation reaction of COD was studied. The kinetic constant and undegradable COD had been calculated. Simulated data tally with experimental data well.

Key words: SBR, biological technique, internal decomposition, bamboo pulp, black liquor, biological degradation, sequencing batch reactor.

Study on the Formula of Expansion Characteristic of Three-phase Biological Fluidized Bed. Pan Tao, Wu Yangshan, Wang Shaotang

(Beijing Municipal Research Academy of Environmental Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 34_37

The formula of expansion characteristic in the three-phase biological fluidized bed has been founded in this study. When the empty-bed velocity of liquid and gas as well as the thickness of bio-film are known, the high of bed expansion is determined rather precisely, which provided basis for design. It is unusual that the expand ruler in both the two-phase bed and three-phase fluidized bed are reflected by using one equivalent function; the relationship of the dynamic in biochemical reaction and behavior of hydromechanics has been set up by the thickness of bio-film. The behavior of shrink in bed under the low velocity of gas can be reflected by this formula, and the formula in three-phase bed can be restored to one in two phase bed when the velocity of gas is zero. The tested bed is 1.4m of diameter and 6.5m of high, in which the diameter of media made of quartz sand is 0.3—0.5mm, using air jet for aeration inside the reactor. The test is within the bio-film thickness of 52, 80, 115, 137m, respectively. The BOD₅ concentration in the sewage tested are 47.6—77.2mg/L.

Key words: three-phase biological fluidized bed, rate of expansion, formula based on experimental data, equivalent function, thickness of bio-film, method for design, wastewater treatment.

Study on the Operation Characters of a Modified Two-Phase Anaerobic Digestion System. Guo Yanghao, Men Chun, Shi Xianai et al. (Dept. of Biotechnology, Fuzhou University, Fuzhou 350002): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 38_40

In this work the operation characters of the two-phase anaerobic digestion system incorporated by a packed bed acidification reactor and an UASB methanorization reactor were studied. The packed bed acidification reactor started up easily and possessed of a high acidification rate and a good resistance against hydraulic impulsion and pH fluctuation. The COD volume charge was higher than 200 kg/(m³·d). Adopting a preadjusting alkalinity technology, the two-phase system could operate normally and effectively for treating brewing wastewater. Under the conditions of COD concentration 1000—7000 mg/L in the feed and COD charge 40 kg/(m³·d), the COD concentration was less than 200 mg/L in the effluent. The system possessed also a rather good capacity for treating antibiotics wastewater.

Key words: packed bed acidification reactor, two-phase anaerobic digestion system, brewing wastewater of high concentration.

An Investigation of the Subjective Response to the Traffic Noise of an Elevated Highway or