

它们的逸出有较大的脉冲性,颗粒污泥容易被上逸的气泡顶出反应器。这样不仅会出现污泥大量流失而影响反应器的处理效率(因为反应器的处理效率与污泥浓度成正相关),而且还影响水质。更为严重的是,沼气的大量积累还会在膨胀床内形成气泡断层,使反应器的机械运行难以持续。试验观察发现,要使生物颗粒污泥流态化,床层膨胀率需保持在 10% 以上。要达到此膨胀率,一般需要回流来加快消化液在反应器中的流速。

但在水力负荷较高时(达 $4\text{m}^3/\text{m}^2\cdot\text{d}$),反应器自身的作用已能使生物颗粒污泥流态化。装置可以停止回流,以节省动力能耗。

三、小 结

1. AAFEB 工艺不但适用于模拟有机污水的处理,同样也适用于实际工业有机废水的处理。用其处理 COD 为 3808—13770 mg/L 的杭州啤酒厂糖化废水的效率参数为: HRT 6h; 容积有机质负荷 $33.76\text{ kg COD}/\text{m}^3\cdot\text{d}$, 容积产气率 $13.90\text{ m}^3/\text{m}^3\cdot\text{d}$, COD 去除率 86.88%, 物料产甲烷率 $0.34\text{ m}^3/\text{kg}$ 去除 COD, 接近其理论值 $0.35\text{ m}^3/\text{kg}$

去除 COD, 沼气的甲烷含量 58—72%。在 HRT 缩短至 3.5h 的条件下, 容积有机质负荷可增加到 $74.01\text{ kg COD}/\text{m}^3\cdot\text{d}$, 容积产气率达 $20.25\text{ m}^3/\text{m}^3\cdot\text{d}$ 。

2. 结果分析表明, 该工艺稳定运行的适宜有机质负荷约 $40\text{ kg COD}/\text{m}^3\cdot\text{d}$; 适宜 HRT 为 6h。

3. 反应器出水碱酸比与装置的稳定运行密切相关。当该比值大于 3.0 时, 装置的运行性能良好; 当此参数小于 3.0 时, 运行性能迅速恶化。

4. 要使反应器正常运行, 床层膨胀率需控制在 10% 以上, 若进水与沼气的作用不足以使生物颗粒污泥流态化, 则需回流。反之则以不回流为好。

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生物水解法处理尿素废水

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一、概 述

尿素合成反应中, 每生成 1mol 尿素同时生成 1mol 水, 加上其它工艺过程排出的水, 化肥厂每生产一 t 尿素大约要排放 0.5—0.7t 工艺废水, 其中含有 1—2% 的尿素, 2—5% 的氨。通常先将这股水进行解吸以回收

一部分氨, 然后再排放。但排放的水中仍含有 0.05—0.07% 的氨, 0.5—1% 左右的尿素。据统计, 我国现有化肥厂仅这一项排水每年损失十几万吨氨。大量含氮物质排入水体造成环境污染。

目前较为成熟的治理方法是以斯太米卡邦 (Stamicarbon) 技术为基础的热力水解

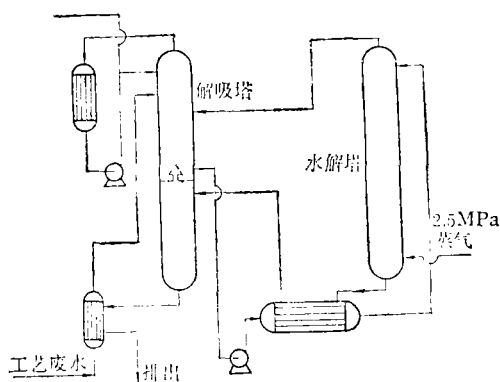


图1 热力水解工艺流程

法^[1] (图1)。在高温 (180—200℃), 高压 (1.6—1.8MPa) 下将水中的尿素水解为 NH_3 和 CO_2 , 然后再进行解吸以回收氨。最先进的技术可使处理后的废水含尿素、氨均小于 10ppm^[2,3], 但这一方法设备庞大, 需使用特种不锈钢, 因而一次投资较高。中压蒸汽 (2.5MPa) 消耗量大, 操作成本高, 我国中小型化工厂蒸汽供应不足, 无法采用这一技术。针对上述操作成本高的缺点, 国外又相继开发了脲酶水解法^[4], 催化水解法^[5,6], 但目前尚不成熟。离子交换法只适于处理低浓度尿素废水^[7], 亚硝酸盐法^[8]将尿素转变成 N_2 , 在经济上不够合理。

二、生物水解的设想及理论依据

在污水处理中广泛采用生物技术, 因为生化处理是最经济的方法之一。如果尿素废水采用生物处理, 既可保留脲酶法在常温常压下操作, 动力消耗低的优点, 又不必进行酶的分离和固定, 从而克服脲酶成本高, 技术难的缺点。

在自然界, 特别在土壤中有许多微生物都含有尿素酶, 在一定条件下, 这些微生物都可以使尿素水解成 NH_3 和 CO_2 ^[9]。尿素水解这一过程, 对于微生物而言不产生能量, 要使微生物保持正常的生命活动还必须提供适当的营养源。因此, 究竟选用哪种微生物应

从技术经济考虑。

好氧微生物的生命活动需供给氧气, 即需要曝气。这样无疑要增加动力消耗。而厌氧微生物对有机物分解不彻底, 如通常处理废水的厌氧消化, 生物降解产物是甲烷。甲烷气的存在对氨的回收利用有影响。兼性厌氧反硝化菌可利用 NO_3^- 中的氧进行呼吸, 不必曝气, 呼吸的产物是氮, 有机营养物则氧化成 CO_2 。它们对氨的回收利用无影响, 因此用反硝化菌作为尿素水解的主要微生物是有利的。另外, 从化肥厂的实际情况出发, 无论用硝酸废水, 还是硝酸尾气, 向尿素废水引入 NO_3^- 或 NO_2^- 都很方便。甲醇是反硝化菌最好的有机碳源, 而化肥厂一般都有一定数量的甲醇废水排出, 恰作为有机物的补给, 而且在选用反硝化菌来处理尿素废水的同时, 还处理了硝酸废水和甲醇废水。

根据这样的设想, 我们安排了试验。

三、试 验

通过选育, 我们获得了适于工业应用的反硝化菌。在此基础上, 首先开展了用反硝化菌水解尿素的静态试验。

将配制的含尿素 1000 mg/L、 NH_4NO_3 3000mg/L、及适量甲醇的水样 2000ml 投入 2500ml 的磨口瓶中, 接入 200ml 反硝化菌液, 混匀后放入培养箱, 在 $27 \pm 1^\circ\text{C}$ 条件下静置 96h。取样分析: NO_3^- -N 去除 80%, 尿素全部去除, 游离氨则由 0 增至 1070mg/L。进而把尿素浓度提到 1500 mg/L 和 2000mg/L, 实验条件相同, 尿素也全部去除, 游离氨分别增至 1340mg/L 和 1630mg/L。由于本试验投配的是 NH_4NO_3 , 在反硝化作用下每去除 1 mol NO_3^- 就增加 1 mol 的 NH_3 , 从试验数据可以看出 NH_3 的增加量与反硝化及尿素水解有定量的关系, 可以说明尿素去除是由于水解生成氨。这一试验结论表明, 用反硝化菌来处理尿素是可行的。

在静态试验基础上, 我们又在软纤维填

料滤床上进行了 8 个月的连续动态试验。试验装置如图 2。含有不同浓度的尿素废水用泵打入生物滤床,滤床为有机玻璃制成,内径 $\phi 75\text{mm}$,高 $H = 850\text{mm}$,内装 7 根腈纶纤维填料,调节泵的流量可控制废水在床内的停留时间。不同停留时间,不同进水浓度的试验结果见表 1。

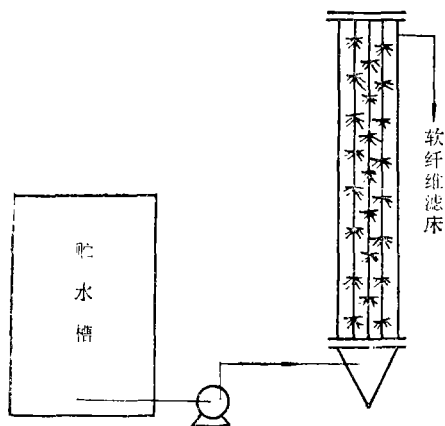


图 2 尿素生物水解试验装置

从表 1 所列数据可以看出,在同样进水浓度下,延长停留时间可以提高尿素的水解率。在同样停留时间下,进水尿素浓度越高,水解越不彻底。

从表中还可以看到,尿素水解比反硝化占优势,并且对反硝化有抑制作用。当废水中不含尿素时,停留 3h, 450mg/L 的 NO_3^--N 去除率大于 99%。当废水中含有尿素时, NO_3^--N 去除率显著下降。这可能是由于尿素水解使废水中氨的浓度增高的缘故。据文献报道^[10]游离氨对反硝化有抑制作用。这对处理尿素废水是有利的。尿素生物水解时反硝化作用减弱,意味着有机物及 NO_3^--N 的消耗较低。经测定,在正常情况下每去除 1 kg 的 NO_3^--N ,产泥量为 $0.16\text{—}0.23\text{kg}$ 。由此推知,水解 1kg 尿素产泥量约为 $0.04\text{—}0.06\text{kg}$,表明产泥量很低,给污泥处理带来了方便。在我们连续 8 个月的试验运转中没有进行排泥而床体保持了正常运行。

表 1 尿素生物水解试验结果

试验日期	床温 ($^{\circ}\text{C}$)	停留 时间 (h)	尿 素 (mg/L)		NO_3^--N (mg/L)	
			进水	出水	进水	出水
	28—30	3			495	3
					457	3
					458	4
6.24	30—32	12	1820	4	345	4
30			1780	5	340	2
7.8			2080	3	263	5
7.28	31—33	12	2940	2	224	25
8.2			3120	13	272	72
4			3200	6	240	115
8.14	31—33	9	2700	98	273	41
18			3340	15	267	32
20			3300	10	275	48
9.5	31—33	3	1000	2	548	287
8			1010	3	557	264
11			950	2	551	89
11.26	30—32	3	1470	69	158	97
12.3			1670	73	213	126
5			1810	25	211	131
12.11	30—32	3	2850	108	221	93
12			2900	104	220	84
15			3170	125	277	103
12.22	30—30	3	4950	280	226	103
25			5140	420	281	119
26			5100	400	280	127

尿素水解过程中活性污泥增长缓慢,因此,在生物水解装置投入运行前应 先 通入 NO_3^--N 及甲醇废水,以便污泥大量增殖。当污泥浓度达到一定值时再投入尿素、 NO_3^--N 、甲醇混合废水。

四、尿素生物水解的工艺流程 及经济性

根据小试结果,我们提出生物水解法处理尿素废水的工艺流程,如图 3 所示。尿素水解产生的氨经解吸塔解吸出来,再回收利用。

根据对兰化化肥厂所排废水的调查,其

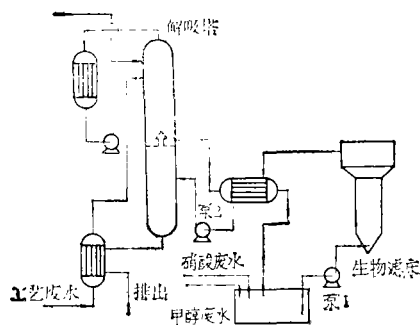


图 3 生物水解工艺流程

中尿素废水含尿素 5000—8000 mg/L, pH 10.3—11.3; 硝酸废水中含 $\text{NO}_3\text{-N}$ 1000—1500 mg/L, pH 2—3; 甲醇废水 COD 为 2000—7000mg/L. 在此以前我们用甲醇废水作为反硝化营养物。试验结果表明: 每去除 1kg $\text{NO}_3\text{-N}$ 可去除 3.5—4.0kg COD. 因此, 上述三种水可按如下比例混合, 尿素废水: 硝酸废水: 甲醇废水 = 5:3:3. 这样的比例基本满足生化反应的需要。

生物水解法与热力水解法相比, 由于在常温常压下操作, 对设备材质要求不高, 对设备结构的要求也简单, 这样可节省许多基建费用, 其操作费用也比热力水解法(图 1) 低得多, 其主要操作单元的动力、材料消耗对比见表 2。

表 2 水解单元动力消耗对照

方法	热力水解法	生物水解法
项目		
蒸汽消耗* (kg/t 废水)	72.5 ($p = 2.5\text{MPa}$)	—
电耗** (kW · h/t 废水)	0.653 (泵压 1.8MPa)	0.048 (输送泵 1) 0.319 (输送泵 2)

* 引自镇海化肥厂设计数据。

** 按 75% 效率计。

通过分析对照, 可以看出生物水解法在技术经济上具有一定的优越性。

五、结论和意见

8 个月的试验证实了我们当初的设想, 并得出如下结论:

1. 采用反硝化菌来处理尿素废水在技术上是可行的。现阶段试验结果表明, 进水尿素浓度为 5000mg/L, 停留 3h, 水解率大于 90%, 体积负荷为 $36\text{kg}/\text{m}^3 \cdot \text{d}$ 。

2. 采用反硝化生物水解法, 可以实现尿素废水, 硝酸废水, 甲醇废水的同时治理。尤其适合综合性化肥厂采用。

3. 本方法污泥产量低, 因而管理方便。

4. 初步核算, 该法基建投资低, 操作费用省, 是一种在技术经济上具有优越性的处理方法。

如果改进生物反应器的形式, 设法提高污泥浓度, 有可能进一步提高体积负荷, 缩短停留时间。

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Chemical Engineering, Shanghai University of Technology, Shanghai)

This work is designed to explore the regularity of organic and heavy metal pollutants released from re-suspended sediment in the Suzhouhe River of Shanghai, and to propose the classification standard of sediment on the basis of surface water quality standard. The proposed standard is classified into nonpollution, pollution and heavy pollution by comparing each of chemical parameters. Pollution assessment was done for the Suzhouhe River according to the standard. It is showed that when the sections of heavily polluted sediment are cleaned up, the sediment would no longer influence on water quality in the Suzhouhe River. (See pp. 26—30.)

Buffering Mechanism of Soil for Acidic Precipitation

Liao Bohan and Li Changsheng (Research Center for Eco-Environmental Sciences, Academia Sinica)

Buffering mechanism of soil for acidic precipitation is an important topic in studying the effects of acidic precipitation on soil. Based on simulation of leaching experiments of acidic precipitation for some forest soils in China, this paper brings forward a discussion about the buffering mechanism of soil for acidic precipitation. The soil consumes H^+ ion through releasing cations, the total amount of released cations is equal to the total amount of consumed H^+ ion in soil. The buffering mechanism of soil consists of three processes, which are the exchange of cations, hydrolysis of aluminum hydroxide, and weathering of primary minerals. The importance of each process is different in various conditions. (See pp. 30—34.)

The Structure and Function of Microbial Population ZE-1 for Decolouring Dyeing Wastewater

Qian Bing, Ye Junying and Xu Guanghui (Zhejiang Institute of Microbiology, Hangzhou); Min Yijue and Shen Yuru (Zhejiang Institute of Environmental Protection, Hangzhou)

The principal purpose of this work is to explore the composition and activeness of microbial population ZE-1 which is able to decolour dyeing wastewater of silk goods more effectively. Ten strains of bacteria were isolated from the samples collected from experimental dyeing wastewater and ten strains from pilot plant dyeing wastewater of silk goods. The results showed that the composition of microbial population ZE-1 consisted of genera of *Bacillus*, *Acinetobacter*, *Achromobacter* and *Pseudomonas* essentially. In microbial population ZE-1 conserved in the lab, the dominant bacteria were *Bacillus* and *Acinetobacter*, which occupied 80% of total number of the isolates. The more effective species or strains decolouring dyeing wastewater microbial population ZE-1 were *Bacillus subtilis* and

Acinetobacter calcoaceticus, *Aeromonas punctate* and *Pseudomonas* No. 19 isolated from pilot-plant samples were effective too. (See pp. 35—38)

Interaction of Carbofuran and Activity of Soil Microorganisms in Paddy Field

Huang Xin, Fan Dejiang and Chen Hexin (Research Team of Pesticide Residues, Zhejiang Agricultural University, Hangzhou)

An attempt was made to understand the biological degradation of Carbofuran in paddy soil and its effect on some microbial activities in soil. The results showed that the degradation of Carbofuran in paddy soil was affected by both biological factors and non-biological factors. Degradation of the pesticide had been retarded by the glucose at concentration of 1% during the early period, though the loss of the pesticide was accelerated during the late period. However, glucose at concentration of 0.1% did not retard degradation of Carbofuran.

Carbofuran at the concentration of 50ppm or more stimulated the degradation of cellulose in four types of soils. The ammonification increased significantly in silty loam while decreased in saline polder soil, when treated with high concentration of Carbofuran (500ppm). (See pp. 38—43)

Treatment of Brewery Saccharification Waste water with the Anaerobic Attached Film Expanded Bed Reactor

Zheng Ping et al. (Department of Environmental Science, Zhejiang Agricultural University, Hangzhou)

In this paper AAFEB reactor is considered to treat brewery saccharification wastewater. When influent COD concentration was 3808—13770 mg/L, operating temperature 28°C, HRT 6 hours, volumetric COD loading rate 33.76 kg/m³·day, the percentage of COD removal attained 86.88% and volumetric biogas production rate 13.90 m³/m³·day. Per kg COD removed produced 0.34 m³ of methane. When HRT was shortened to 3.5 hours, volumetric COD loading rate reached 20.35 m³/m³·day. The critical bed expansion was about 10% and critical ratio of alkalinity to acidity about 3.0 (See pp. 44—48)

Treatment of Urea-Plant Wastewater by Biological Hydrolysis

Cui Lianqi, Ji Biliang and Li Yaqi (Institute of Environmental Protection, Lanzhou Chemical Industry Co., Lanzhou)

Results of the experiments show that denitrifying bacteria were able to hydrolyze urea in the wastewater into CO₂ and NH₃ which could be recovered under suitable conditions. Sources of NH₃ or organic matters in the waste-

water came from the products of HNO_3 or CH_3OH . Using the biological reactor filled with fibre, 5000 mg/L urea in the influent was hydrolyzed by 93% in 3 hours, meanwhile 280 mg/L NO_3^- -N was reduced to 120 mg/L. (See pp. 48—51)

Treatment of Cr(VI) Aqueous Solution by Liquid Membrane with Sulfoxides as Carriers

Ding Mei et al. (Research Center for Eco Environmental Sciences, Academia Sinica, Beijing)

Extraction of Cr(VI) by liquid membrane has been studied. DOSO and PSO were used as carriers. The related factors i.e. type and amount of the surfactants, quantity of carriers, concentration of NaOH, volume ratio of oil phase and that of internal phase, acidity of external aqueous phase and temperature were studied in bench-scale experiment. The optimization of technological operative factors were obtained in intermittent experiments. Based on this research, the authors considered the graph of state distribution of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} in aqueous solution under various pH values and infrared spectra of free DOSO and the extrated species of Cr(VI), the Cr(VI) extraction mechanism by liquid membrane with DOSO is proposed as follows:

Complexing: $\text{DOSO} + \text{H}^+ + \text{HCr}_2\text{O}_7^- \rightleftharpoons \text{DOSOH}^+ \cdot \text{HCr}_2\text{O}_7^-$ Freeing: $\text{DOSOH}^+ \cdot \text{HCr}_2\text{O}_7^- + 4\text{NaOH} \rightleftharpoons \text{DOSO} + 2\text{Na}_2\text{CrO}_4 + 3\text{H}_2\text{O}$ (See pp. 52—55)

Analysis of Anisokinetic Sampling Errors for PM10 (Particulate Matter $\phi < 10\mu\text{m}$)

Zhou Yao (The Chinese Academy of Prevention Medicine, Beijing)

Isokinetic sampling is called the in-stack sampling which is different from ambient air sampling. The PM10 in-stack sampling is rather difficult as a fixed flow is used in PM10 sampling. In this article, two methods, varied from the nozzle size and EGR(Exhaust Gas Recirculation) method, have been introduced. Anisokinetic sampling er-

rors and their limits which are caused by the former one have been emphasized. Meanwhile, some other factors which cause errors such as numbers of sampling point and angles of sampling nozzle are briefly illustrated.

(See pp. 56—58)

Toxicity of Seven Environmental Toxicants to the Bacteria *E. coli* as an Indicator

Dai Jisen et al. (Hunan University of Medicine, Changsha)

Agar plate method has been used to observe toxicity of Hg, Cd, Pb, As, Cr, phenol and cyanide toward the indicating bacteria *E. coli*. The result is that sensitivity of *E. coli* to the seven chemicals is $\text{Hg} > \text{Cd} > \text{Pb} > \text{As} > \text{Cr}$ and the inhibition zones of phenol and cyanide have not been seen. *E. coli* used as a kind of indicating bacteria to detect industrial sewage is suitable for the sewage containing metals.

Analysis of regression is taken with the concentrations of Hg, Cd, Pb and As to each mean diameter of inhibition zone, and each correlation coefficient has high significant level, the regression slopes are $\text{As} > \text{Cd} > \text{Hg} > \text{Pb}$. The analysis of regression may provide evidence for further research. (See pp. 59—61)

Study on Relationship of BOD₅ and COD in Accordance with Biochemical Theory

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This paper based on biochemical theory focuses on relative mechanism between BOD₅ and COD, and has established a relevant mathematical model which is linear in form. The authors have proposed an assessment formula for the biochemical reaction of wastewater, and so has proved fine relativity between BOD₅ and COD to use water quality data of the Suzhouhe River of Shanghai. (See pp. 62—66)