微电解 - 生化组合工艺处理氯丁橡胶生产废水*

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摘要 采用微电解 - 水解 - 厌氧 - 好氧生化新工艺对氯丁橡胶有机废水进行中试,结果表明,在中试稳定运行时,废水 COD 总去除率可达 97.6 %,出水 COD 平均浓度在 300 mg/L 以下。
关键词 微电解 生化工艺 氯丁橡胶废水 中试处理

0 引言

氯丁橡胶是由氯丁二烯聚合制成的合成橡胶,强度高、耐磨性好、抗氧化、耐油且抗老化,获得广泛的应用。但在生产过程中产生大量有机废水,污染物浓度高,废水中主要含乙炔、乙醛、二乙烯基乙炔、氯丁二烯、二甲苯等,属于难降解有机废水。目前对于其它橡胶废水的处理研究较多[1-8],但对于氯丁橡胶废水的处理研究报道较少[9]。

本试验采用微电解、生化、混凝等多单元组合工艺处理氯丁橡胶废水,规模为 3 m^3/d,通过 3 个月的试验,处理效果基本达到了设计要求,出水满足行业排放标准。

1 材料与试验

1.1 废水来源

根据生产废水的实际情况,中试试验的混合废水是由生产废水按一定的比例混合而成,其水质见表 1。

表 1 中试混合废水水质 g/L(pH 除外)

COD	BOD_5	SS	LAS	pH
13.0～15.0	4.0～6.0	3.5～7.5	10～15	6.8～7.2

1.2 试验工艺流程

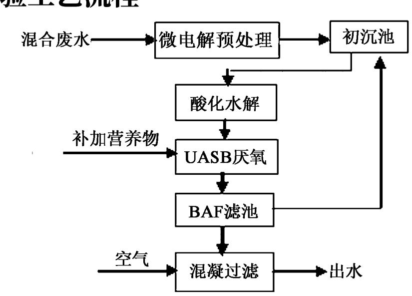

图 1 中试工艺流程示意图

1.3 菌种驯化及培养

接种污泥取自大同市西郊污水处理厂,添加培养基,逐步加入废水,7 d 为 1 周期重复培养,提高菌液浓度作为水解(酸化)单元用。

1.4 试验方法

(1) 操作条件的确定。本试验首先在实验室试验的基础上对各单元反应器的操作运行条件进行确定,包括微电解预处理及各单元的进水 COD 浓度、生化温度、水力停留时间、pH 值试验条件(见表 2)。

(2) 长期稳定运行。各单元按表 2 进行了长期的运行试验,运行过程中每隔一定时间取样,测定进水,反应器清液和系统出水的 COD 浓度变化及其它指标。

表 2 试验运行条件

试验项目	进水 COD/ (g·L^{-1})	生化温度/ ℃	停留时间/ h	pH 值
水解池	12.0～13.0	35	24	8.0
厌氧罐	7.0～8.0	38	24	8.0
氧化池	2.0～2.5	20～25	12	8.0

2 试验结果与分析

2.1 微电解预处理结果

利用铁屑进行微电解预处理。利用铁的还原作用、微电解作用、混凝吸附作用使得废水中的 COD 降低 20 %左右。

2.2 水解(酸化)反应结果

2.2.1 水解(酸化)反应的启动调试

经过前处理后的废水,过滤铁屑进入水解池进行启动调试,向池中投加浓度为 500 g/L 已培养好的优势菌液 300 kg,之后废水以 2.0 g/L 浓度进行生化反应,1 周后连续进水,间断地调整进水浓度,投配负荷以流量为 120 L/h 进水,水解(酸化)反应的启动运行结果见图 2。

从图 2 可以看出,在水解(酸化)反应池中 COD

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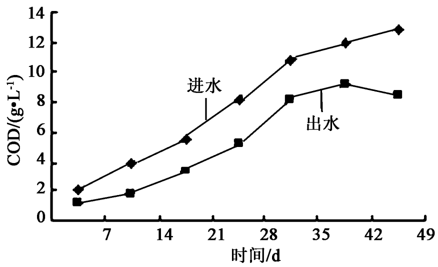

图 2 水解池中进出水 COD 浓度变化

去除率为 40 %左右,显示出 COD 去除率不高,其主要原因是废水中有机物转化成各种有机酸等小分子物质,但废水的可生化性大幅度提高,在此期间出水 COD 浓度维持在 7.0 g/L 左右,挥发酸(VFA,以醋酸计)在 2.0 g/L 左右。

2.2.2 负荷调试运行结果

在提高负荷运行中,控制进水 COD 浓度 2.0～13.3 g/L,进水 COD 负荷约 12.4 kg/(m^3·d),COD 容积负荷均 4.75 kg/(m^3·d),高时可达 6.13 kg/(m^3·d),系统指标达到一个较好的水平,如图 3 所示。

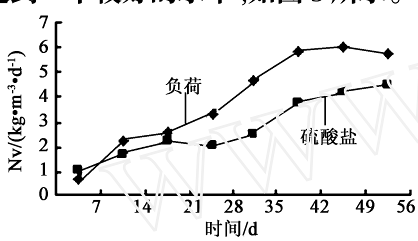

图 3 水解(酸化)容积负荷及硫酸盐随时间变化

2.3 厌氧反应结果

2.3.1 厌氧反应调试阶段

厌氧段采用 UASB 工艺,活性污泥呈颗粒状,沉降性能良好。启动调试时,向反应器中投加 300 kg 接种污泥及稀释后浓度为 2.0 g/L 的废水,间歇培养 7 d,以 120 L/h 的流量连续进水,COD 的容积负荷由 0.25 kg/(m^3·d)增高至 2.0 kg/(m^3·d),逐步将进水 COD 浓度提高到 7.0 g/L 以上。

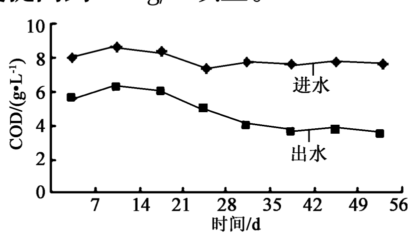

图 4 厌氧调试运行 COD 浓度随时间变化

从图 4 可知,运行出水 COD 浓度维持在 3.5 g/L 以下,pH 值为 7.0,COD 去除率可达 47.3 %,经絮凝可使厌氧出水 COD 降至 3.0 g/L 以下。

2.3.2 厌氧反应负荷调试

厌氧反应进水 COD 负荷为 4.0 kg/(m^3·d),容积负荷为 3.1 kg/(m^3·d),整个厌氧反应的调试运行阶段,由于厌氧污泥对废水逐步适应,微生物生长迅速,反应器底部形成颗粒污泥,其 SVI 值为20.2 mL/g。通过在清水中沉降试验表明,颗粒污泥沉降速度约为 20 m/h,说明污泥沉降性能好,通过显微镜观察,污泥中产的甲烷细菌主要是甲烷杆菌,具有较高的稳定性和较强的机械性。

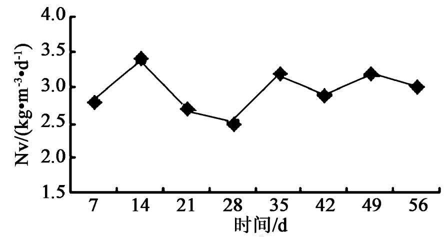

图 5 厌氧容积负荷随时间的变化

2.4 好氧反应结果

在厌氧反应器启动期间,好氧反应池同时进行内循环挂膜和驯化接种污泥,在反应池中投加 300 kg 浓缩污泥,然后逐步加入厌氧消化后的废水,最后进水 COD 浓度为 3.0 g/L,闷曝培养,2 d 后继续进水运行,结果见图 6。图 6 可知,控制厌氧段出水 COD 浓度为 2.5 g/L,进水 COD 浓度为2.0 g/L,出水达标。中试挂膜过程 1 个月,在随后的运行过程中,随厌氧反应器出水浓度波动使好氧反应池出水浓度也呈现较大变化,之后则逐渐趋于稳定,出水 COD 浓度为1.5 g/L,去除率达 58.3 %。

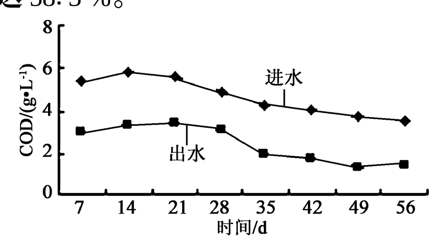

图 6 好氧运行 COD 浓度随时间的变化

2.5 全工艺运行结果

全工艺各单元经过 3 个月的调试运行后,出水各项指标趋于稳定,全工艺稳定运行 20 多天平均结果见表 3。由表 3 可见,稳定运行出水 COD 未达到行业排放标准。为了改变这一状态,结合化工橡胶废水的特点,本试验采用了复配混凝后处理工艺,最后使出水 COD 浓度在 300 mg/L 以下。

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2.86 g/g[4]。而实际测得 COD 降解量与 NO_3^--N 降解量的比值 $\Delta S_{COD}/\Delta S_{NO_3^--N}$ = (174.00 - 94.00)/(31.84 - 5.71) = 3.06。结果表明,反应过程中 NO_3^--N 降解量与对应的 COD 降解量的比值大于理论值。分析产生偏差的主要原因是:(1)在试验过程中,由于是实际城市污水,混合液中多少会有分子态溶解氧作为电子受体消耗了溶解态的 COD;(2)原水中一部分可生物降解的有机物转化成了细胞物质;(3)原水中还有一些有机物属于难生物降解性的,在测定反硝化速率试验过程中未被代谢利用。

3 结论

(1)反硝化过程中存在 3 个速率明显不同的反硝化速率阶段,且随着反应时间的延长,反硝化速率逐渐降低。第 1 阶段反硝化速率最大,其反硝化速率值为 13.09～20.20 mg/(g·h),所需反应时间为 12～30 min;第 2 阶段反硝化速率次之,反硝化速率值为 4.24～5.55 mg/(g·h),反应时间在 60～130 min;第 3 阶段反硝化速率最小,反硝化速率值为 1.91～3.44 mg/(g·h),反应时间为 40～80 min。

(2)城市污水厂进水水质变化对反硝化过程影响较大。研究得到的反硝化速率值和反应时间可作为城市污水厂缺氧选择池、生化反应池缺氧区工艺设计计算时参考。

(3)由于试验过程存在偏差,实际测得的反硝化过程中 NO_3^--N 降解量与对应的 COD 降解量的比值大于理论值。

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表 3 稳定运行 21 d 出水 COD 平均结果

项目	水解出水	厌氧出水	好氧出水	混凝
COD/(mg·L⁻¹)	6 690	3 670	1 520	294
去除率/%	43.5	54.9		9.7
总去除率/%		87.2		97.6

注:原水 13～15 g/L,预处理11 830 mg/L。

3 结论

(1)水解(酸化) - 厌氧 2 级运行条件为,温度 35～38 ℃,水力停留时间 24 h,进水浓度为 12.0 g/L;好氧单元可在常温下进行,设计进水 COD 浓度控制在 2.0 g/L 以下,水力停留时间 12 h。

(2)水解(酸化)单元添加优势复合菌对去除 COD 具有显著效果,经水解(酸化) - 厌氧 2 级处理 COD 去除率 87.2 %,厌氧单级反应器负荷 3.1 kg/(m³·d),系统平均去除负荷达 4 kg/(m³·d),再经过好氧处理,该废水 COD 总去除率达 97.6 %。

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POWDER ACTIVATED CARBON-MEMBRANE BIOREACTOR FOR TREATMENT OF MUNICIPAL WASTEWATER ……… *Pei Liang Yao Binghua* (7)

Abstract The combined process of powdered activated carbon (PAC) and membrane bioreactor (MBR) was applied for treatment of municipal wastewater. The removal efficiencies of COD, NH_4^+-N and turbidity in the combined process were investigated. The result showed that the combined process may achieve better removal efficiencies of COD, NH_4^+-N and turbidity, when water temperature is above 26 ℃, DO is above 4.5 mg/L and pH is between 6 and 9. The average removal efficiencies of COD, NH_4^+-N and turbidity in the combined process were 88 %, 98 % and 98 % respectively, and was better than that of single MBR process and conventional process. The effluent COD was less than 22 mg/L and NH_4^+-N was less than 1 mg/L, turbidity was less than 1NTU. It was better than that of water for domestic reuse stated by the Ministy of Construction (CJ25.1 - 89). The fouled membrane was cleaned by water rinsing, water-acid rinsing, water-alkali rinsing, which can let its flux be restored to 43 %, 81 %, 89 % of a new membrane respectively.

Keywords powder activated carbon membrane bioreactor domestic wastewater

INACTIVATION OF MICROBE IN RUNNING WATER USING MICROWAVE ELECTRODELESS ULTRAVIOLET LIGHT ……… *Lou Chaogang Xia Dongsheng Zhao Fan et al* (10)

Abstract E. coli and Bacillus subtilis were selected to express respectively the easily and difficultly inactivated microbe, and the best irradiation time and the limit turbidity of microwave electrodeless ultraviolet (UV) irradiation were studied. In this condition, checking the disinfection of E. coli and Bacillus subtilis, and compared with mercury lamp of medium pressure. The results showed that when best irradiation time was 210 s, microwave electrodeless ultraviolet irradiation can achieve inactivation rate of 99.92 %. In order to obtain the best results of disinfection effect, the water of turbidity was below 8 NTU, the limit turbidity of disinfection was 40 NTU; microwave electrodeless ultraviolet irradiation can achieve inactivation rate of 100 % with 180 s, and the Bacillus subtilis inactivation rate of 100 % with 300 s, it is more effective than mercury lamp of medium pressure disinfection.

Keywords E. coli Bacillus subtilis limit turbidity drinking water disinfection efficiency electrodeless UV lamp

STUDY ON THE BULKING SLUDGE IN THE PROCESS OF SHORT RANGE NITRIFICATION OF HIGH AMMONIA WASTEWATER ……… *Hou Qiaoling Wen Yibo Li Linbao et al* (13)

Abstract A/O technique was used to treat simulated high ammonia wastewater, the stability short-cut nitrification could be implemented by controlling the right content (accumulation rate ≥80 %), the activated sludge had good settling property, in the late of the short-range nitrification it was degraded gradually. It is showed by the experimental results that increasing N/P ratio in the wastewater can slightly drop SVI, but still can not effectively ease the sludge bulking. The bulking sludge would be occurred when COD load was above 0.27 kg/(kg·d). Controlled DO with 1.5 to 2.0 mg/L, the solid-liquid separation result is good, and the removal rates of NH_4^+-N and COD, as well as the cumulative rate of nitrite nitrogen are greater than 90 %, sludge bulking can be effectively controlled.

Keywords short-range nitrification sludge bulking A/O process

TREATMENT OF WASTEWATER CONTAINING Cr(Ⅵ) BY PVA MICRO-BALL ENTRAPPED IRON POWDER AND ACTIVATE CARBON ……… *Huang Yi* (15)

Abstract Micro-ball entrapped iron powder/activate carbon was prepared by liquid-liquid phase separation method and its effect on treating the simulation wastewater containing Cr(Ⅵ) was investigated. The results showed that the removal rate of Cr(Ⅵ) could reach 99.7 % at pH value of 2 and treating time of 4 h. The effluent could reach the discharge standard of China, the treatment operated steadily and the iron powder and activate carbon did not agglomerate in the continuous removal process. So this method is superior to the common iron-carbon micro-electrolytic method.

Keywords entrapping method iron powder activate carbon Cr(Ⅵ)

TREATMENT OF NEOPRENE WASTEWATER WITH MICROELECTROLYSIS AND THREE-UNIT BIOCHEMISTRY PROCESS ……… *Zhang Sheng Xu Lirong Zhu Jianrong et al* (18)

Abstract A pilot study on the treatment neoprene wastewater with integrated microelectrolysis and three-unit biochemistry process was done. The experiment results under the stable condition showed that COD removal rate was up to 97.6 %, COD concentration of the effluent could be reduced to less than 300 mg/L.

Keywords microelectrolysis three-unit biochemistry process neoprene wastewater treatment of pilot scale

DEGRADATION OF SAFRANINE T BY THE TECHNOLOGY OF CATALYTIC OXIDATION ……… *Wang Lijuan Huang Jiguo Dong Lili et al* (20)

Abstract The technology of catalytic oxidation is studied for degrading safranine T. The self-made polyoxometalate $Zn_{1.5}PW_{12}O_{40}$ nanotube is used as the catalyst and dioxygen is used as the oxidizer. The results show: $Zn_{1.5}PW_{12}O_{40}$ is sutiable for catalyst, with the structure of the $Zn_{1.5}PW_{12}O_{40}$ being hollowed, the type of the $Zn_{1.5}PW_{12}O_{40}$ being affiliated to the type of heteropoly acids, and the scale of the $Zn_{1.5}PW_{12}O_{40}$ being nanometer-scale; in the oxidation system of air, the optimum reaction time is 4 hours, and correspondently the degradation rate and the degradation velocity are respectively 78 % and 665 μg/h; the activity and stability are both high, and when the circulation times are four, the degradation is still 65 %.

Keywords nanotube dioxygen safranine T degradation rate circulation