

污水的光化学灭菌处理研究

孔令仁 陈 曦 杨 曦 马文漪

(南京大学环境科学与工程系, 南京 210093)

摘要 以日光和中压汞灯为光源, 以亚甲基兰(下简称 MB)为光敏剂, 研究了南京市某污水样的灭菌处理和从灭菌水样中除去 MB 的方法. 结果表明: 光源、光强、光照时间、MB 用量和溶解氧等因素对灭菌有显著影响; 不加 MB 的水样经紫外光(下简称 UV)灭菌后, 在日光下细菌呈现复活(下简称光复活); 当 1L 细菌总数为 3.1×10^6 个/ml 的污水加入 2mg MB, 并在充气状态下以 300 W 中压汞灯光照 4 min, 其灭菌率达 100%, 且无光复活; 同样条件下日光的灭菌率则低很多; 水样中残余的 MB 用膨润土可有效除去.

关键词 光化学, 光敏化剂, 紫外辐射, 灭菌.

确保水环境中微生物数量的安全性直接关系到人类健康. 目前, 对于饮用水、生产和生活用水、医疗和生化处理后污水的灭菌虽然有许多化学方法, 但这些方法都各有利弊^[1].

1977 年, Acher 等人首先采用光敏化法灭菌^[2]. 该方法在 UV 灭菌的基础上, 利用光敏化剂在可见光下产生多种形式的活性氧, 大大提高了灭菌率和光的利用率, 同时减少了细菌的光复活. 1985 年, 首次利用日光光敏化进行污水灭菌处理的实验工厂在美国田纳西州投入运行^[3]. 1990 年, 另一座类似的处理工厂也在以色列建成^[4], 展示了该方法的实用性.

我国人均水资源贫乏且分布不均, 污水再生利用在一些地区已刻不容缓. 因此, 在日光能充足和水源紧缺地区, 开发光敏化技术灭菌将有良好前景. 该方法国内尚未见报道, 本文旨在探讨影响光敏化对污水灭菌的各种因素, 建立主要以日光为光源的光敏化方法, 为该技术的实际应用提供依据.

1 实验部分

1.1 仪器和试剂

NDC- 型光化学反应仪和 300W 中压汞灯(南京大学环境科学与工程系研制)^[5], PIX 型生化恒温培养箱(沈阳分析仪器三厂), 888 型加压气泵(南京东山电器厂).

MB 配成 0.5% 使用液, 膨润土(150 目以下)也配成 0.5% 悬浮液, 用前充分振荡.

1.2 测试方法

细菌测试方法见《水和废水标准检验法》^[6], 采用 SPC 法, 做 3 个稀释度, 每样 4 份平行. MB 用分光光度法测定, 波长为 530nm.

1.3 实验步骤

(1) 采样 所取南京市某水样为生活和工业混合污水, pH 为 6.5, 水温 15℃, 细菌总数 $10^5 - 10^6$ 个/ml, 水样保存于 4℃ 冰箱内.

(2) 日光光敏化 在 9 份 200ml 水样内加入 MB 使用液, 使 MB 浓度分别为 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 和 5.0mg/L. 水样置于盖有表面皿的 250ml 烧杯中, 用充气泵连续充气, 并在日光强度为 2.1×10^4 lx 下照射 40 min. 与此同时, 配制相同 MB 的污水系列置于暗室中, 充气, 作为暗对照试验. 取样测定细菌总数.

(3) 日光照射时间 取 2 份 200ml 污水, 其中一份 MB 浓度为 2mg/L, 另一样不加 MB. 水样在 250ml 盖有表面皿烧杯中充气光照, 日光强度为 4.9×10^4 lx. 不同时间取样测定.

(4) 日光强度 取 6 份含 MB(2mg/L) 的污水 200ml 于 250ml 盖有表面皿的烧杯内, 分

别于 1.2×10^4 、 2.1×10^4 、 4.9×10^4 、 5.3×10^4 、 7.3×10^4 和 $8.4 \times 10^4 \text{ lx}$ 日光下照射 40min, 同时连续通气. 照毕取样测定.

(5) 充气 取 2 份含 MB (0.5 mg/L) 的污水 200ml 于 250ml 盖有表面皿的烧杯内, 在日光强度为 $1.2 \times 10^4 \text{ lx}$ 下照射 40min. 其中一份用加氧泵充气, 另一份不充气, 对比溶解氧对灭菌的影响.

(6) 中压汞灯灭菌 开启 NDC- 型光化学反应仪的冷却水和 300W 中压汞灯, 预热 15min 后向反应器内加入 1L 含 MB (2 mg/L) 的污水, 开启充气装置和磁力搅拌器, 在 2、4、6 和 10min 时取样测定. 关灯 10min 后关冷却水. 同时作一份不加 MB 的污水光照灭菌试验.

(7) 光复活试验 取上述中压汞灯灭菌后的水样 200ml 于 250ml 盖有表面皿的烧杯中, 在平均光强为 $7.2 \times 10^4 \text{ lx}$ 日光下照射并于 30 和 60min 时取样分析. 同时作暗对照试验.

(8) MB 的去除 将 4 份含 MB (2 mg/L) 水样 200ml 加入不同量的膨润土使用液, 使膨润土与 MB 之比分别为 4 1、6 1、8 1 和 10 1, 磁力搅拌 15min 后静止过夜. 取上层清液测定 MB 的去除率.

2 结果与讨论

2.1 日光光敏化试验结果

结果见图 1. 曲线 2 表明细菌存活数 N 随 MB 的浓度增大而降低. 日光的 UV 部分几乎被表面皿和烧杯阻挡, 因为 Pyrex 玻璃不能透过 350nm 以下的辐射. 在此条件下, 灭菌仅依靠 MB 的光敏化作用. 暗对照试验显示细菌的

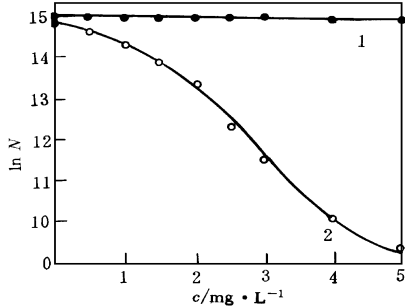


图 1 MB 浓度对灭菌的影响

存活数无变化 (见曲线 1), 表明 MB 需在光照条件下才有光敏化作用.

2.2 光照时间对灭菌的影响

试验结果见图 2. 曲线 2 表明细菌存活数随时间增加而减少, 因为体系接受的光能与光照时间成正比. 同时也可以看出, 不加 MB 的对照试验其细菌数几乎不随时间改变 (见曲线 1), 这也是没有 MB 的光敏化作用所致.

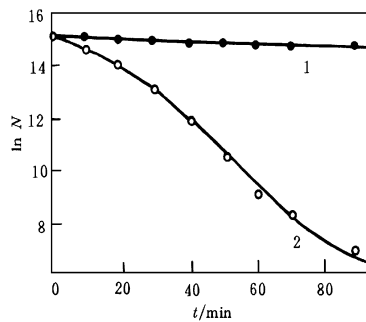


图 2 日光照射时间对灭菌的影响

2.3 光强对灭菌率的影响

图 3 显示光强 I 对灭菌率的影响. 光强大, MB 产生的活性氧 ($^1\text{O}_2$) 多, 灭菌率高. 这与光化学反应速率正比于光强是一致的.

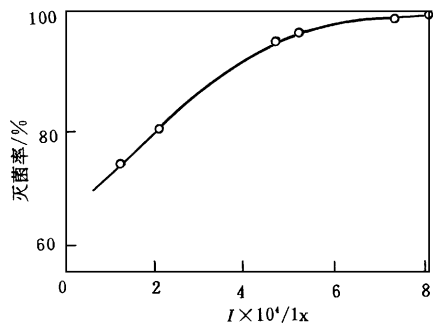


图 3 日光强度对灭菌率的影响

2.4 充气对灭菌率的影响

充气试验使细菌数为 1.2×10^5 个/ml 污水的灭菌率达 95.9%, 而相同条件下不充气的灭菌率仅为 81.5% (见图 3). 充气增加了污水中的溶解氧, 有利于在 MB 作用下生成 $^1\text{O}_2$.

2.5 中压汞灯的灭菌效果

与日光相比, 中压汞灯的灭菌效果更好. 在加入 MB 的试验中, 污水样光照 2min 后的灭菌率达 99.9%, 4min 后达 100%. 中压汞灯发

出的光谱范围广(表 1), 其灭菌作用首先是可见光对 MB 的光敏化; 其次是在 NDC- 型光化学反应仪内由于石英器皿能透过中压汞灯的 UV 而使细菌直接受到辐射伤害^[1]. 同样条件下不加 MB 的对比试验需要照射 8min 才能使灭菌率达到 100%, 显然是没有光敏化作用所致.

表 1 中压汞灯的主要波长和相对强度

波 长/nm	相对强度
1367. 3	15. 3
1014. 0	40
557. 0- 559. 0	76
546. 1	93
405. 0- 407. 8	42. 2
365. 0- 366. 3	100
296. 7- 334. 1	99. 7
270. 0- 289. 4	22
253. 7- 265. 5	37. 9

2. 6 光复活试验结果

试验结果见表 2. 表明仅用中压汞灯灭菌, 然后在日光下细菌呈现光复活. 在此条件下细菌受到伤害主要是 UV 作用, 有关光复活机理已有许多报道^[8]. 但是, 若体系中存在 MB, 细菌则同时受到¹O₂ 的伤害, 其氧化过程和产物在日光下是不能逆转的. 表 2 也显示, 光照灭菌后污水置于暗处, 细菌几乎不出现复活.

表 2 日光下细菌的光复活结果

复活 时间 / min	细菌光复活数/ 个 · ml ⁻¹			
	中压汞灯灭菌后		中压汞灯+ MB 灭菌后	
	日光下	暗处	日光下	暗处
0	0	0	1	1
30	20	1	3	2
60	300	0	10	2

2. 7 MB 的去除结果

膨润土对 MB 的去除是有效的. 结果表明, 在膨润土与 MB 的重量比为 4 : 1 时, 去除率为 84. 1%; 大于 6 : 1 时, 去除率即达 100%. MB 是一种阳离子型染料, 膨润土对它的吸收能力很强, 其吸收量接近于它的阳离子交换量^[2].

3 结 语

本试验结果表明, MB 与日光的光敏化作用能有效用于污水灭菌. 由于日光的主要部分(500- 700nm) 与 MB 的吸收范围很好重合, 光敏化效果明显. 同时, 中压汞灯和日光都发出 UV, 可直接损害细胞组织. 光敏化后剩余的 MB 能用膨润土去除.

参 考 文 献

1 Larson R A. Biohazards of Drinking Water Treatment. USA: LEWIS. Publishers Inc. 1989:iii- vi

2 Acher A J. Dye-sensitized-photo-oxidation a New Approach to the Treatment of Organic Matter in Sewage Effluents. Water Res., 1977, 11: 557

3 Eisenberg T N, Middlebrook E J et al.. Sensitized Photooxidation for Wastewater Disinfection and Detoxification. Water Sci. Technol., 1987, 19: 1255

4 Acher A, Fecher E et al.. Photochemical Disinfection of Effluents-pilot Studies. Water Res., 1990, 24(7): 837

5 孔令仁等编. 环境化学实验. 南京: 南京大学出版社, 1989: 137- 141

6 宋仁元等译, 美国公共卫生协会等编著. 水和废水标准检验法(第 15 版), 北京: 中国建筑工业出版社, 1985: 744- 748

7 Larson R A, Berenbaum M R. Phototoxicity. Environ. Sci. Technol., 1988, 22(4): 354- 360

8 武汉大学、复旦大学生物系微生物教学研究室编. 微生物学(第二版). 北京: 高等教育出版社, 1987: 290- 291

Changchun 130023), Xu Aijun et al (Chinese North-east Institute of Municipal Engineering Design, Changchun 130021): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 38- 41

The Mn^{2+} removing activity of the filter sand from 2 Chinese Water Plants was analyzed to determine the role of the bacteria in the Mn^{2+} removing Procession. Enumeration of bacteria on PYCM medium showed that there were 10^5 - 10^6 bacteria per g wet sand and about 40% - 50% of the colonies had the ability to oxidize Mn^{2+} . By the in situ enrichment of the bacteria, sterilization and the $HgCl_2$ inhibition of the mature sand, it was found that bacteria were indispensable to the maintenance of the activity of the sand. When the bacterial activity was inhibited, the activity of the sand was reduced to 20% of the original one. The remaining activity might be due to the chemical catalysis. Bacteria were the major source of the Mn^{2+} removing activity of the filters.

Key words: groundwater, Mn^{2+} , bacteria, chemical factors, filter sand.

A Study on the Characteristics of the Activated Sludge for Anaerobic Attached Microbial Film Expanded Bed Process. Zhang Jianli and Li Lijian (Dept. of Food Science, Laiyang Agricultural College, Laiyang 265200), Feng Xiaoshan (Dept. of Environ Science, Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 42- 44

The characteristics of activated sludge in the anaerobic attached microbial film expanded bed (AAFEB) reactor were studied. The results showed that there were three consecutive phases in the course of biofilm formation and development, namely, adsorption phase, partly coating phase and fully coating phase. In this process, the predominant microorganisms were changed gradually from coccus to filamentous organisms, which caused anaerobic sludge activity increasing. Under the acidification condition, there were a lot of streptococcus and extracellular polymer on the surface of activated sludge, and the sludge activity was low.

Key words: anaerobic attached microbial film expanded bed reactor, anaerobic activated sludge, biofilm.

Catalytic Properties of Two Kind of Catalysts in Toluene Combustion Reaction. Li Shiyao, Li Shulian et al. (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 45- 47

Toluene organic exhausts were regarded as index reaction in evaluating the catalytic performance of honeycomb ceramic monolith catalysts consisting of noble metals and non-noble metals respectively by means of a continuous system with a fixed bed of catalysts. The effect of toluene concentration and oxygen content in the exhaust, space velocity, linear velocity on toluene

reaction, and the thermal stability of catalysts were investigated. It is found that the activity of noble metal catalyst is superior than that of non-noble metal catalyst under different conditions. The light-off temperature of toluene exhaust on non-noble metal catalyst is by 50 °C higher than that on noble metal catalyst after catalysts calcine at 600 °C for 3h. Meanwhile, after catalysts calcine at 900 °C for 3h, the light-off temperature of toluene exhaust on noble metal catalyst increases only by 3 °C as compared with the calcination of 600 °C for 3h. But under same condition, the light-off temperature of toluene exhaust on non-noble metal catalyst increases by 87 °C.

Key words: combustion reaction of toluene exhaust, honeycomb ceramic monolith catalyst, thermal stability, light-off temperature.

Photochemical Disinfection of Wastewater. Kong Lingren, Chen Xi et al. (Dept. of Environ. Sci. and Eng., Nanjing University, 210093): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 48- 50

A new method of photochemical disinfection for wastewater from Nanjing city was investigated. By aerating and using methylene blue (MB) as photosensitizer, the wastewater samples were disinfected under sunlight and a medium pressure mercury lamp separately. The results were as follows: (1) The disinfection of wastewater were remarkably affected by the light sources, light intensity, irradiated time, MB concentration and dissolved oxygen; (2) The bacteria which were disinfected by UV could be partially photoreactivated under sunlight; (3) The disinfection rate could reach 100% and the bacteria photoreactivation were not appeared when 1 liter of the sample containing 3.1×10^6 bacteria and 2 mg MB were irradiated by a 300W medium pressure mercury lamp for 4 min; (4) The residual MB in the samples could be removed by bentonite clay. The disinfection mechanisms of UV and photosensitization, the bacteria photoreactivation and the effects for affecting disinfection were discussed.

Key words: photochemistry, photosensitization, UV irradiation, disinfection.

Summary of Studies on the Ecology of Lake Donghu. Liu Jiankang and Huang Xiangfei (Institute of Hydrobiology, Chinese Academy of sciences, Wuhan 430072): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 51- 53

Taking the Donghu (in Wuhan), a representative lake of the middle and lower basins of Chang Jiang River as a base, the present project has conducted stationary monitoring and systematic researches on the ecology of Lake Donghu for more than 30 years. Achievements of the studies include the estimation of the budgets for the main nutrients nitrogen and phosphorus of the lake, as well as their distribution and accumulation in