几种偶氮染料生物降解性研究

全　燮　杨凤林　李和平*
（大连理工大学环境工程研究所）

摘要　用改进的 Bunch 和 Chambers 的静态生物培养技术研究了五种偶氮染料的生物降解性. 结果表明，这些染料在厌氧条件下容易降解，在好氧条件下降解速率很慢. 厌氧降解时偶氮基断裂生成胺基物. 降解速率的大小与染料的结构及取代基的种类和数目有关.

关键词　染料;生物降解.

随着染料工业的迅速发展，染料的品种和数量日益增加，由各种途径进入周围环境的染料废水直接或间接地危害人类的健康. 据统计全世界每年约有 640000 吨染料产品，品种达几万种. 仅我国目前试制和生产的染料就有五百多种. 人工合成的染料具有一定程度的毒性，其中有的染料毒性较强，生物降解性差. 尤其是染料降解中间体的毒性强，严重地污染环境. 全世界每年以废弃物形式向周围环境排放的染料约 60000 吨左右[1]. 这些染料废水一般采用混凝法-生物法进行二级处理. 但是由于缺乏单一染料生物降解性的基础数据，缺乏对染料生物降解机理的认识，目前对染料废水的生物处理具有一定程度的盲目性，所以生化处理装置不能充分发挥其效力. 染料生物降解性的研究不仅对揭示染料在环境中的行为具有意义，而且能为正确选择合理的生物处理方案提供理论依据. 国际染料生产工业的生态和毒理协会（ETAD）的主要研究方向之一，就是研究染料的生物降解性. 世界各国也正开展这方面的工作[2-4].

本文实验研究了五种偶氮染料的生物降解性，初步探讨了其降解机理.

一、实验部分

1. 实验材料

酵母汁，BOD 稀释水，生活污水，染料.

2. 主要仪器

锥形瓶，72-1 型分光光度仪，岛津 LC-4A 高效液相色谱仪，高压蒸汽灭菌器，生物培养箱.

3. 实验步骤

培养液的配制：在培养瓶中加入一定量的酵母汁，染料，用 BOD 稀释水稀释. 体系中染料的浓度为 10mg/L.

生物培养：采用 Bunch 静态培养技术. 将培养瓶放入 25℃ 恒温生物培养箱内，定期取样分析，测定体系中染料和氧浓度.

产物的鉴定：将培养液样品高速离心，取清液用高压液相色谱仪分析.

二、结果与讨论

1. 五种染料的结构与物性

本实验所选用的五种染料，在结构上的共同特点是都含有偶氮双键（—N=N—）. 可用通式 R—N=N—R′ 表示. 具体结构式见表 1.

2. 好氧与厌氧条件下染料的生物降解性

本实验采用 Bunch 和 Chambers 建立的静态培养技术. 该法曾被美国环保局（EPA）用于优先污染物生物降解性的实验研究[5]. 法此具有要求设备简单，可以同时得到微生物降解性和对微生物驯化难易数据

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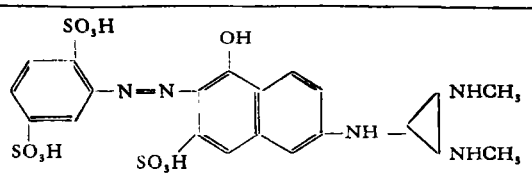
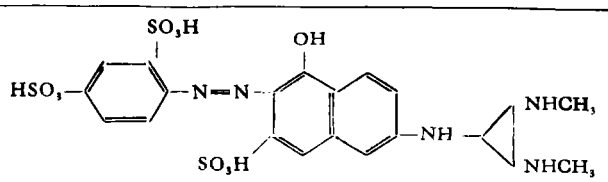
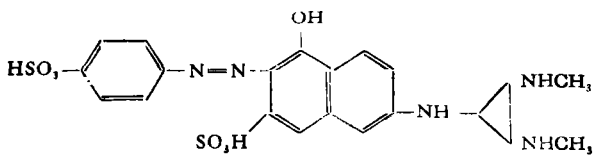
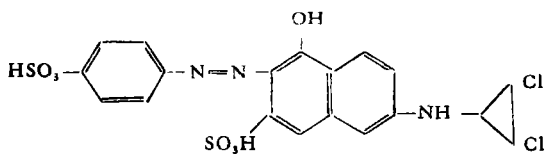
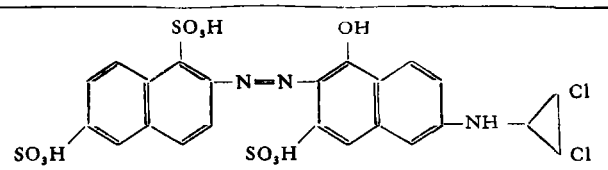
* 一九九〇年应届毕业生

表 1 五种染料的结构式

代 号	染料种属	结 构 式
JM-1	酸性染料	
JM-2	酸性染料	
JM-3	酸性染料	
J-3	活性染料	
J-7	活性染料	

的优点.

在实验初期,采用对培养液充氧的方法,使培养体系在染料降解过程中给微生物的生长提供足够的氧. 在充氧条件下 (初始氧浓度 8.6 mg/L), 酵母汁浓度 50, 1000, 1500 mg/L 三种情况下的生物降解实验表明, 只有酵母汁为 1500mg/L 的条件下, 染料才能被降解; 其他两种酵母汁浓度下染料浓度均无变化.测定三种情况下的溶解氧浓度,发现 1500mg/L 酵母汁浓度下培养液中氧浓度在 24 小时内变为零, 而 1000mg/L 和 50mg/L 时, 七天后培养液的氧浓度分别为 3.2, 7.8 mg/L (见表 2). 从以上的结果可以推测染料似乎是在厌氧条件下容易降解. 当酵母汁浓度为 1000mg/L、50mg/L 时, 七天后培养液中溶解氧仍然存在,即仍处于好氧状态,染料无明显降解. 但当酵母汁浓度为 1500 mg/L 时, 较高浓度的酵母汁不仅提供了微生物生长所需的营养, 而且自身耗氧给体系提供了厌氧环境,染料明显降解.

表 2 充氧时几种情况下溶解氧浓度*

实验条件	酵母汁 1500 mg/L (1d 后)	酵母汁 1500 mg/L (7d 后)	酵母汁 50mg/L (7d 后)	酵母汁 1000mg/L (7d 后)
溶解氧 (mg/L)	0	0	7.8	3.2

* 初始溶解氧均为 8.6mg/L

为了证实以上的推测, 采用加热法驱除

培养液中的溶解氧，然后加入 1000mg/L 的酵母汁进行实验．结果表明，在该条件下染料能被降解．以 JM-2 为例，七天后的降解率为 70.6%．由此可以认为，实验所用五种染料在厌氧条件下容易降解，但在好氧条件下降解速率很慢．

3. 五种染料的生物降解性与结构的关系

五种偶氮染料生物降解实验结果绘成图

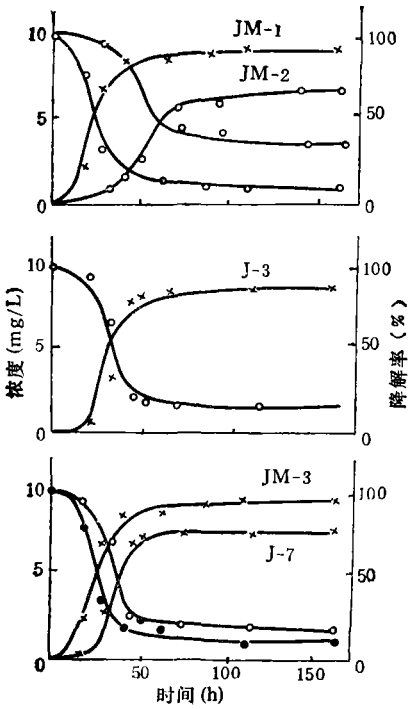


图 1　五种染料生物降解曲线

实验条件：酵母汁浓度 1500 mg/L，染料浓度 10mg/L，厌氧环境．按 Bunch 和 Chambers 的评价方法，将染料按七天生物降解率的大小排成如下顺序

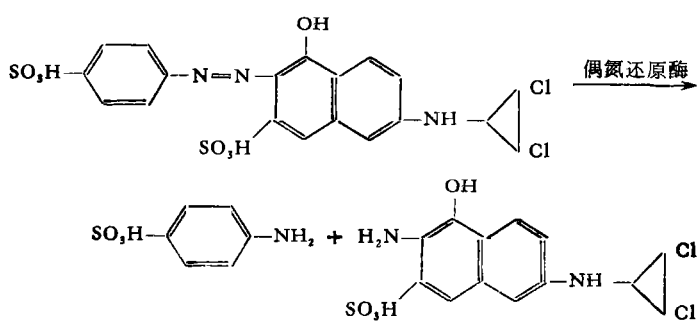
JM-3 > JM-1 > J-7 ≈ J-3 > JM-2

从染料的结构上，将上述降解率大小顺序解释如下：JM-1、JM-2 和 JM-3 三种染料的偶氮基相同，区别在于重氮基上磺酸基的位置和数目不同，前两者在重氮基上有两个磺酸基，JM-3 只有一个磺酸基，而 JM-1、JM-2 的生物降解率均小于 JM-3．前期对几种活性偶氮染料的生物降解性的研究也发现了同样的规律．可见增加磺酸基的数目不利于微生物降解．从三种染料的降解率数据可以看出，偶氮基对位上有磺酸基时，对染料降解的不利影响较小．换言之，间位和邻位上存在磺酸基时，比对位上有磺酸基影响更大．

JM-3 与 J-3 相比，前者的降解速率快，两者七天生物降解率相差 10.5%．从结构上看，两者的母体结构相同，只是 J-3 偶氮基上的氯被甲胺基所取代．从降解数据可知，带甲胺基的 JM-3 比带氯基的 J-3 易降解．

4. 降解产物的鉴定与降解机理的推测

为了鉴定降解产物，将 J-3 降解后的培养液经高速离心机离心后取上清液进行了高效液相色谱分析（见图 2）．鉴定出对胺基苯磺酸，测其含量为 3.0mg/L．从 J-3 的结构式算出如果 J-3 全部降解，可生成 3.5mg/L 的对胺基苯磺酸．可见 3.0 mg/L 的对胺基苯磺酸相当于 85.7% 染料降解率所对应的量．该值与实测值 84.9% 基本一致．由此可以推测如下的降解机理：



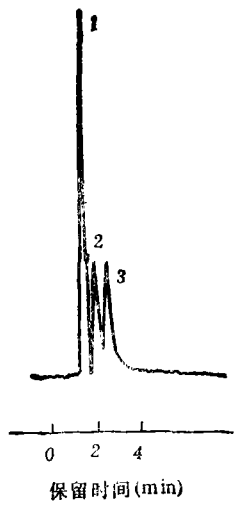


图2 降解产物的高效液相色谱图
1.对胺基苯磺酸 2.3.未鉴定峰

上述反应是降解的第一步反应。产物在适当的条件下可进一步降解。但从第一步反应的产物对胺基苯磺酸的浓度分析，在厌氧条件下对胺基苯磺酸的进一步降解速率很慢。可见，在厌氧条件下，生物降解过程基本停留在第一步降解阶段。

三、结 论

1. 五种偶氮染料在厌氧条件下容易降解，在好氧条件下降解速率很慢。

2. 五种染料的生物降解性与结构有一定的关系，当母体结构一致时，重氮基上磺酸基数目多不利于降解。磺酸基在偶氮基对位时比在其他位置时容易降解。偶氮基上末端环中的氯被甲胺基取代时更易生物降解。

3. 五种染料在厌氧条件下，偶氮双键被微生物作用而断裂形成胺。生成的胺在厌氧条件下进一步降解速率很慢。

因此，偶氮染料废水首先应厌氧生化处理。

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醋酸纤维素小孔径超滤膜的研究*

王静荣 刘廷惠
(中国科学院生态环境研究中心)

摘要 用醋酸纤维素 (CA) 为聚合物材料，研制出了截留分子量 2000—10000、对 PEG 截留率为 90% 以上的小孔径超滤膜。并就铸膜液组成，制膜条件及膜的透过特性等进行了实验。

关键词 醋酸纤维素；超滤膜；α-干扰素。

近年来，超滤分离技术发展很快，已研制出了多种高分子材料的超滤膜。醋酸纤维素 (CA) 超滤膜国内研究较早，也是目前应用较广泛的一种。但是，CA 小孔径超滤膜国内研究甚少，未见文献报道。

由于 CA 膜的 pH 适用范围较窄，易生物降解、不耐高温等缺点，在某些应用上受到限制。但 CA 膜的亲水性较其它膜材料好，

* 冯宝和同志参加了部分工作。

Abstracts

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This paper introduces the purifying efficiency of separating surface-active wastewater by foam. In the experiments, sodium dodecylsulfate (SDS) was reduced from 31.5—183.0 mg/L to 3.4—45.7 mg/L by batch separation, and from 75—200 mg/L to 11.2—65.2 mg/L by continuous separation. Use of a four-stage separation could result in concentration of SDS from 100 mg/L in solution to 20 g in foam.

Key Words: foam, surfactant, purication efficiency.

Study on Biodegradability of Some Sorts of Azo-Dyestuffs. Quan Xie, Yang Feng-lin, Li Heping (Research Institute of Environmental Engineering, Dalian University of Technology): *Chin. J. Environ. Sci.*, **12**(3), 1991, pp. 27—30

Biodegradability of five azo-dyestuffs was studied with the static bio-cultural procedure of Bunch and Chambers. The results showed that the dyestuffs were so easy to be degraded under anaerobic conditions that azo-group could cleave to be aniline sulfonic acid, but under aerobic conditions their decomposition was very slow. The magnitude of degradable rates depends on the dyestuff structure and substituent species and numbers.

Key Words: azo-dyestuff, biodegradation.

Preparation of Small-Porous Ultrafiltration Membrane with Cellulose Acetate. Wang Jing-rong, Liu Ting-hui (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing): *Chin. J. Environ. Sci.*, **12**(3),1991, pp. 30—33

The paper deals with preparation of ultrafiltration membrane which intercepts the matter of molecular weights 2000—10000 and by which interception rate of PEG is over 90%. The components of the membrane, processing conditions and its penetrative characteristics have been tested.

Key Words: cellulose acetate, ultrafiltration membrane.

Experimental Study of the Relationship between Total Organic Carbon (TOC) and Biochemical Oxygen Demand (BOD). Huang Chang-zhu (Nanjing Municipal Research Institute of Environmental Protection): *Chin. J. Environ. Sci.*, **12**(3), 1991, pp. 34—36

TOC and BOD are the water-quality parameters for determining organism mass in water. There exists a certain relation between them. Reported in this paper is that by the parallel experiments of biochemical culture, TOC and BOD are equal valence under the meaning of "carbon-containing organisms taking part in oxygen consumption", and both obey one valence kinetic reaction and have the same constant of degradation rate. There is a general linear relation between TOC and BOD by the coefficient a of oxygen consumption for TOC and indegradable mass b for BOD: $BOD = a(TOC - b)\cdot\exp(-5k_1)$

Key Words: total organic carbon (TOC), biochemical oxygen demand (BOD), relationship.

The Experimental Study of Decolorization of Dyeing Wastewater Treated with M-Ferrites as A Catalyst. Jie Wen, Xu Hui-ping, Liu Jianrong (Department of Environmental Engineering, Taiyuan University of Technology): *Chin. J. Environ. Sci.*, **12**(3), 1991, pp. 37—41

Reported in this paper is an experimental study that M-ferrites were used as a catalyst to treat dyeing wastewater for decolorization by the catalysis of air oxidation. the catalysts were a series of M-ferrites which were composed of different components. It was found that Ni-ferrite had a good capacity for catalyst decolorization towards the wastewater containing insoluble reductive dyes, and its decolorized rate was over 90%. The results of infrared spectrum analysis indicated that the catalyst Ni-ferrite for decolorization reaction to the insoluble reductive dyeing wastewater was reacted with complete oxidation of the auxiliary, sodium hydrosulphite ($Na_2S_2O_4$) in the wastewater so as to convert the dye into insoluble sediment, which then was separated.

Key Words: dying wastewater, decolorization, M-ferrites, catalyst.

Photochemical Treatment of Wastewater Containing Dichromate and Cyanide. Xu Yi-ming, Chen Xiaoliang (Department of Chemistry, Yangzhou Teachers College, Jiangsu Province): *Chin. J. Environ. Sci.*, **12**(3), 1991, pp. 41—45

The factors which influence on the photocatalytic reduction of dichromate and the photocatalytic oxidation of cyanide have been studied in this paper. In the process of photocatalytic reduction of dichromate, the catalytic activity of semiconductor (TiO_2, WO_3 etc) is dependent not only on its nature, but also on the preparation method of semiconductor. Surface modification of catalysts by platium can substantially increase their photocatalytic activity. The process of dichromate photoreduction is also influenced by acidity of solution and the presence of ferric ions and methanol. The process of photocatalytic oxidation of cyanide ions is more efficient if the cyanide solution contains H_2O_2. From the viewpoint of practical application, a photochemical apparatus with TiO_2-coated or TiO_2-zeolite-coated photoreactor has been designed for treating wastewater continuously.

Key Wrods: dichromate, cyanide, semiconductor catalysis, photoreduction, photooxidation.