染料在好氧条件下的生物降解性能

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摘要 根据合成染料的特性选用了较简单易行的3种生物降解性能测定方法,即静置烧瓶筛选试验法,瓦勃氏呼吸仪法,半连续活性污泥法试验,对26种染料进行了测定分析,并比较了3种方法的结果和原因。同时,就环境因素对有机物生物降解性能测定的影响作了简要讨论。结果表明,多数染料在好氧条件下是难降解的,半连续活性污泥法试验虽然需较长的时间,但较另2种方法准确。

关键词 染料,好氧,生物降解性能

好氧生物法能够经济有效地去除一般有机物,但对染料废水的处理效果往往不够理想,脱色差,对于难降解的染料更无效果。目前已有不少有关染料生物降解性能的研究报道,主要集中在简单偶氮染料[1],对其它结构的染料还缺乏较系统的研究。

1 材料和方法

1.1 材料

本试验选用的染料有三苯甲烷类5种,含杂环的偶氮染料7种,还有三偶氮、蒽醌、酞菁及各种杂环结构染料共26种,上述染料均可溶于水。

1.2 方法

(1)静置烧瓶筛选试验[2] 以10ml沉淀后的生活污水作接种物,90ml含有5mg酵母膏和适量被试物的BOD稀释水为基质,两者混和并充养后,在室温下静置培养。培养1周后进行测定,并以该培养液作为下一周培养的接种物,如此连续培养4周,共28d,同时进行已知可降解化合物的对照试验。

(2)瓦勃氏呼吸仪试验 用瓦勃氏呼吸仪,利用压差技术测定活性污泥中微生物利用有机物及其自身内源呼吸耗氧的变化,比较内源呼吸耗氧曲线和有机物耗氧曲线(生化呼吸线),以此来判断有机物的生物降解性能。如果某有机物的生化呼吸线在内源呼吸线之上,表明该种有机物可被生物降解;而若生化呼吸线低于内源呼吸线,说明该有机物不能被生物降解,且对微生物有抑制作用;如果两线重合,表明有机物不能被降解,但对微生物无抑制作用[3]。

(3)半连续活性污泥法[4] 取污水处理厂的活性污泥置于曝气装置中,加入受试物及经过沉淀的生活污水,曝气23h,然后停止曝气,沉淀污泥并弃去上清液;留在曝气装置中的污泥和再次加入的等量受试物及污水混和,重复上述步骤,并通过测定上清液中COD及染料浓度的变化来判定生物降解情况。试验污水用人工配制的COD:N:P=100:5:1的葡萄糖溶液。

2 结果与讨论

2.1 静置烧瓶试验

试验中生物降解难易程度以下列数据为准:

染料降解率>70%,易降解;40%—70%,可降解;20%—40%,降解性差;<20%,难降解或不可降解。

试验结果如表1。

从表1可看出,多数染料均难降解,在几种可以降解的染料中,除了直接橙S、直接绿GN外,其余几种染料的降解率均有一些波动,初始培养时降解率较大,第一次培养后有所下降,以后又逐渐升高,可能是因为微生物对降解产物逐渐适应的结果。

对照物苯酚的结果,以及对接种物的细菌计数表明,接种物中含有足够的微生物。

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表1　静置烧瓶染料生物降解性试验结果[1)]

染　料	各次培养后降解率(%)				降解性能评价		备注
	初始培养	第一次再培养	第二次再培养	第三次再培养	降解性能	驯化难易	
苯酚	80	100	100	100	好	易	对照物
直接橙 S	23.8	27.4	26.6	25	差	难	
直接绿 GN	15.8	16.2	19.6	18.5	差	难	
酸性墨水蓝 G	58.7	63.7	35.7	35.3	差		非生物影响大
碱性品绿	82.6	82.9	82.2	80.3	好	易	非生物影响大
碱性品蓝 BO	38.5	21.8	26.6	32.1	差	难	
碱性品红	59.6	46.8	45.9	46.5	好	难	
阳离子蓝 x-GRRI	62.6	41.4	41.9	32.8	差	难	
直接耐晒嫩黄 5GL	0	0	0	0	难降解	难	非生物影响大
直接耐晒翠蓝 GL	0	0	0	0	难降解	难	
碱性桃红	7.8	0	2.9	0	难降解	难	
弱酸蓝 BRN	0	0	0	0	难降解	难	
酸性胡蓝 A	9.3	1.8	0	0	难降解	难	
酸性玫瑰红 B	0	0	0	0	难降解	难	
酸性嫩黄 2G	2.1	0	0	0	难降解	难	
酸性媒介藻蓝 B	0	0	0	0	难降解	难	
酸性媒介桃红 3BM	0	0	0	0	难降解	难	
活性嫩黄 2G	0	0	0	0	难降解	难	
活性黄 KRN	0	0	0	0	难降解	难	
活性艳橙 KR	0	0	0	2.5	难降解	难	
活性红 M-8B	0	0	0	0	难降解	难	
活性翠蓝 KN-G	2.6	6.7	2.5	2.3	难降解	难	
活性艳红 X-3B	0	0	0	0	难降解	难	
阳离子桃红 FG	0	1.6	3.0	0	难降解	难	
阳离子翠蓝 GB	0	0	0	1.6	难降解	难	

1) 染料浓度为 20mg/L,降解率为去除非生物影响后的值

2.2　瓦勃氏呼吸仪试验

试验测定了各种染料在3个浓度下的降解性能,试验结果分为4类(见表2):

(1)所有浓度样品的耗氧曲线均在内源呼吸线之上,耗氧量随浓度增加而增加,包括碱性品红、碱性品蓝 BO 和酸性墨水蓝 G。这类染料可生物降解。

(2)所有浓度样品的耗氧曲线均在内源呼吸线之上,且耗氧量随浓度的增加略有增长。包括直接绿 GN 和酸性媒介漂蓝 B。这类染料虽可生物降解,但降解性较差。

(3)各种染料浓度的耗氧曲线均与内源呼吸线很接近,耗氧量随浓度大小变化无一定规律,属此类的染料有酸性胡蓝 A、活性翠蓝 KN-G、弱酸蓝 BRN、阳离子蓝 x-GRRL、阳离子桃红 FG、活性艳橙 KR、直接耐晒嫩黄 5GL、活性黄 KRN、和酸性嫩黄 2G。这类染料属于难降解的,但对微生物无抑制性。

表2　瓦呼仪试验结果

染料种数	可降解无抑制	降解性差无抑制	难降解无抑制	低浓度可降解高浓度有抑制	低浓度难降解无抑制高浓度有抑制	有抑制
23种	2种	2种	9种	2种	7种	1种
占总数(%)	8.7	8.7	39.1	8.7	30.4	4.3

(4)染料的耗氧量随浓度增加而降低,低浓度时耗氧曲线接近内源呼吸线,而高浓度时则在内源呼吸线之下,此类染料有直接橙S、活性嫩黄K-4G、酸性媒介桃红3BM、酸性玫瑰红B、阳离子翠蓝GB和活性红M-8B,属于难降解的染料,且对微生物有抑制性。

2.3 半连续活性污泥法

表3为各种染料的试验结果。

表3 各种染料处理运行结果

	染料及降解性	去除率(%)	运行周期(d) 2	3	4	5	6	8	10	11	12	13	14
易降解和可降解	碱性品绿	COD	58.8	77.7	83.6	85.1	86.2	85.7					
		染料		72.8	96.9	100	100	100	100				
	碱性品红	COD				83.7	23.6	93.0	85.7	87.7		85.6	
		染料		99.0	97.4	97.3	85.8	83.1	75.1	68.0	61.8	63.0	62.4
	直接绿GN	COD	85.9		90.6		81.0			85.6		84.0	
		染料	80.6		74.6	74.2	59.8			63.0	62.2	56.2	
	直接橙S	COD	81.5		88.1		76.6			92.0		87.3	
		染料	100		94.3	98.5	92.3			90.3	89.6		
	阳离子蓝x-GRRL	COD	92.2		71.0		77.2			75.6		77.3	
		染料	100		100	100	98.6	100		94.9		100	
	阳离子艳红5GL	COD		81.7	85.5	85.0	84.9	86.3			90.5	90.3	
		染料			64.9	58.0	43.0	37.5	31.4	42.2	44.9	44.3	35.4
降解性差	直接耐晒翠蓝GL	COD		89.6	90.2	88.3	90.2	87.5			89.1	93.2	
		染料			35.1	32.4	34.7	37.3	34.2	42.2	31.6	22.3	36.5
	活性翠蓝KNG	COD				85.1	87.5	88.4	82.5		87.4		
		染料		45.1	27.4	22.7	27.2	19.0	21.7		21.1	20.9	
	酸性媒介漂蓝B	COD	87.8	78.4			81.5				83.7		83.7
		染料	59.0	52.9	45.6		31.2				35.9	26.8	22.6
难降解	弱酸蓝BRN	COD		84.9	85.3	84.1	84.7	85.3			89.8	88.8	
		染料			17.3	8.5	7.5	2.7	0	0	0	1.1	8.1
	酸性胡蓝A	COD				80.1	86.5	90.5	79.7	88.5			
		染料	33.7	16.7	11.4	15.7	11.6	8.5	4.2	11.4	7.7	8.9	
	酸性媒介桃红3BM	COD		77.8	79.4	80.6	81.0	82.0			81.5	81.5	
		染料			25.5	27.8	3.9	0	0	20.4	7.5	13.1	12.4
	活性艳红x-3B	COD		80.3	85.2	88.5	90.2	87.5			89.1	93.2	
		染料			9.8	6.0	5.9	0	0	9.5	0	1.7	5.8
	活性黄KRN	COD				70.5	79.5	81.1	67.5	88.9		85.3	
		染料		0	0	0	0	0	0	0	0	0	
	活性嫩黄KG	COD				85.5	78.9	89.0	81.4	85.0		87.4	
		染料		12.3	1.3	0	2.0	6.7		9.0	9.1	13.4	8.6
	活性红M-8B	COD				85.8	82.6	91.8	82.0	86.7		86.8	
		染料		21.8	12.6	8.3	11.9	10.0		8.0	10.0	8.7	9.3
	活性艳橙KR	COD	83.7	82.8			80.3				83.4		90.6
		染料	10.0	4.3	14.6		0				12.1	5.8	1.9
	阳离子桃红FG	COD	76.0	86.7			77.3				70.2		72.9
		染料	90.9	91.6	88.8		56.8		41.7		18.9	15.8	12.3
	阳离子翠蓝GB	COD	58.4	60.9				59.7			74.7	77.0	75.8
		染料	57.5		11.7			0		0	0	0	0
	碱性桃红	COD	88.4	75.4				60.0			70.8	79.6	77.1
		染料	100		84.2			61.2		49.5	45.0	11.2	10.7
	酸性嫩黄2G	COD	83.6	85.9				80.7			81.0	75.4	85.1
		染料	27.2		13.6			23.1		0	0	0	0

在测定的各类染料中，属易降解的和可降解的染料6种，包括2种碱性染料，2种直接染料，2种阳离子染料；降解性差的有3种，包括直接、酸性和活性染料各1种；难降解的有12种。

吸附对本试验有一定的影响，所有染料在试验开始时都有较大的染料去除率，主要是因为活性污泥的吸附作用，随着试验的进行，吸附逐渐达到平衡；除非染料具有很好的生物降解性能，染料的降解率会逐渐下降直至平衡。

本试验时间为2周，要彻底断定染料的不可降解性显得短了些(目前还不能确定多长时间合适[5])，但各染料在试验后期基本达到了平衡。

2.4　3种方法结果比较

上述3种方法测定结果略有不同，见表4。

表4　3种方法测定结果比较[1)]

染料	静置烧瓶法	瓦呼仪法	半连续活性污泥法
酸性墨水蓝G	(+)	+	
碱性品绿	+	+	+
碱性品红	+	+	+
碱性品蓝BO	(+)	+	
直接橙S	(+)	−	+
直接绿GN	(+)	(+)	+
直接耐晒翠蓝GL	−	−	(+)
阳离子蓝x-GRRL	(+)	−	+
阳离子艳红5GN	−	−	+
酸性媒介漂蓝B	−	(+)	(+)
活性翠蓝KN-G	−	−	(+)
其它	−	−	−

1) "+"表示可降解；"(+)"表示降解性差；"−"表示难降解

表4表明，用活性污泥作接种物，含有易降解物质作为碳源的半连续活性污泥法具有较好的生物降解条件，而另外2种方法除了几种三苯甲烷类的碱性染料可降解和另外一些难降解染料外，其它结果互有交叉。

引起这种不同的原因有：(1)接种物不同，静置烧瓶法用沉淀后的生活污水，菌量相对少得多，瓦呼仪试验用驯化后的活性污泥，而半连续活性污泥法在试验开始时污泥未经驯化；(2)染料浓度不同，静置烧瓶法类似自然水体条件，使用的接种量小，采用低的染料浓度，瓦呼仪试验中染料是唯一碳源，浓度太低会受到限制，采用了较宽的浓度范围，而半连续活性污泥法中染料浓度接近实际染料厂排水；(3)基质不同，静置烧瓶法有少量酵母膏和生活污水，半连续活性污泥法用葡萄糖配水作为碳源，而瓦呼仪试验则只有染料作唯一碳源；(4)理化因素不同，温度、吸附等对不同方法有不同的影响，而且这些条件也不尽相同。

3　结论

(1)在24种试验染料中大部分在静置烧瓶筛选试验中难生物降解，只有酸性墨水蓝G、3种碱性染料、2种直接染料和1种阳离子染料可降解或者降解性差。

(2)瓦呼仪试验中的23种染料多数是难生物降解的，有3种碱性染料易降解，直接绿GN和酸性媒介漂蓝B可降解但降解性差。浓度高时，染料对微生物有抑制作用。

(3)在半连续活性污泥法中，试验的21种染料中有12种难降解，3种降解性差，6种易降解或可降解。

(4)3种方法结果有些不同，其中半连续活性污泥法条件较好。3种试验法采用的染料浓度、接种物、基质和理化因素不同是造成试验结果不同的主要原因。

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Abstracts

experiment, atmospheric monitoring.

Study on the Biodegradabilities of Dyes under the Aerobic Conditions. An Huren (China-Japan Friendship Environ. Protection Centre, Beijing 100029), Qian Yi et al. (Dept. of Environ. Eng., Tsinhua University, Beijing 100084): *Chin. J. Environ. Sci.*, **15**(6), 1994, pp. 16—19

Three simple and practical aerobic biodegradability test methods, i. e., static flask screening test, Warburg respirometry and semi-continuous activated sludge system, were chosen depending on the characteristics of dyes to test the biodegradabilities of 26 water soluble dyes. The results of tests using these three methods were compared and the reasons for the differences between these results were explained. The effects of environmental factors on the biodegradability tests were also discussed. It was found that most of the dyes studied are refractory under the aerobic conditions, and the semi-continuous activated sludge system is a favourable and more precise test method although it takes a longer time.

Key words: dyes, biodegradability, aerobic.

Study on the Mechanism of the Bacteria-added Biological Contact Oxidation Process in the Treatment of Wastewater from Jiemycin Production Process. Luo Guowei and Yang Danqing et al. (Institute of Environ. Sci., South China Normal University, Guangzhou 510631): *Chin. J. Environ. Sci.*, **15**(6), 1994, pp. 20—22

This paper deals with a treatment system in which the "hydrolytic acidification-two staged biological contact oxidation-coagulation" process was used to treat a high strength wastewater from the production process of jiemycin. Particularly, it relates to the characteristics, distribution patterns and degradative functions of its aerobic microbial films. The selection and breeding of efficiently degradative bacteria, and whether or not the added bacteria can keep its dominance in the reactor were also studied to explore the mechanism of treating jiemycin wastewater by using the bacteria-added biological contact oxidation process. By the separation and identification of aerobic microbial films from this system, 18 strains bacteria species in 11 genera were obtained. Their distribution of bacteria counts and the effectiveness of degrading organics show that after passing through a pilot operation the added bacteria still exist in the reactor and take the dominant position, and the most dominant strain was identified to be in *Aeromona*. Both qualitative and quantitative analyses of the effluents from pilot aerobic treatments were made to find the reasons for causing the remaining COD_{Cr} values.

Key words: jiemycin wastewater, bacteria-added biological contact oxidation process, dominant species of bacteria, biodegradability, GC/MS.

Classification of Atmospheric Pollution Areas and Afforestation Models. Zhao Yong and Li Shuren (Henan University of Agriculture, Zhengzhou 450002): *Chin. J. Environ. Sci.*, **15**(6), 1994, pp. 23—27

Based on the monitoring and predictive analysis of atmospheric pollutants, the clustering analytic method and synthetic index method were used to classify the pollution areas into four types and to classify the greening vegetations into three types in terms of the size of index value. Then further based on the features of pollution for each type of pollution areas, corresponding afforestation models and plant species were selected to green the areas in order to improve the atmospheric environmental quality there. The study demonstrates that more serious single and compounded pollutions generally took place at 300 to 4000m leeward from pollution sources, where an afforestation model consisting of the proper combination of arbor, bush and grass was better in improving the quality of atmospheric environment.

Key words: afforestation model, atmospheric pollution, synthetic index.

Study on the Database System for the Biodegradabilities of Organics in Wastewaters. Huang Xia and Jiang Bin (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **15**(6), 1994, pp. 28—32

Based on analyzing in an all-round way the status of demand for the database systems for biodegradabilities of organics in wastewaters and their features, and by using a software engineering method, the systems analysis and systems design of the users-oriented database system have been completed that form a firm basis for further implementing the system.

Key words: wastewater, organics, degradability, database system.

Study on the Electrode Polarization in the Electrolytic Treatment of Lead Wastes Containing Gold and Silver. Zhang Zhongyan, Liang Huqi et al. (Shanghai University of Technology, Shanghai 200072): *Chin. J. Environ. Sci.*, **15**(6), 1994, pp. 33—37

A detailed study, based on the theories of electrochemical thermodynamics kinetics, was carried out on the polarization behavious and process conditions in the electrode processes of separating gold and silver from lead and obtaining a pure lead