利用 DO 在线监测与判断制药废水毒性*

范彩安　彭永臻　潘力军　李利生

提要　以 SBR 为反应器,分别以制药废水和生活污水为基质,有无预曝气为类别,做了两组平行试验。试验中无毒生活污水的 DO 曲线符合常规变化,有毒制药废水的 DO 曲线出现了特有的周期性波动。通过 DO 在线监测与适时取样测定 COD,验证了 DO 可在线监测并定性判断制药废水的毒性。DO 曲线的周期性波动解释为活性污泥微生物解吸与降解底物的周期性交替。在进一步试验中,为得到有毒制药废水的最易辨识的特征 DO 曲线,可采用不同的曝气方式和曝气量以加强、减弱水样毒性对微生物的冲击,使微生物总有一个活性状态能反应 DO 特征周期波动;曝气量过大导致 DO 过高时 DO 特征波动被掩盖。

关键词　制药废水　毒性　DO　COD　周期性波动

0　前言

制药废水是一种特殊的工业废水,不同于生活污水营养均衡;也不同于一般工业废水毒性单一;它的特性不仅表现在因生产原料与产品多样性导致的毒性复杂,更表现在对活性污泥微生物毒性作用的微量高效性 ——衡量药性的一个重要指标。

SBR 处理工艺在 1914 年发明之后的很长一段时间内未得到广泛应用,主要原因是由于其自动化控制要求高。SBR 工艺的运行是完全混合式的流态,但形成的是推流式的浓度梯度,因而不仅对进水水质的波动具有较好的适应性,还可以反映运行中各种条件的影响[1]。因此,用 SBR 作为反应器,并进行其自动控制的基础研究,是有实用性的。

正是源于制药废水对微生物毒性的微量高效性,以及 DO 在活性污泥系统中即时反应微生物活性的特点,本文假设并验证了 DO 可用于在线监测并定性判断制药废水毒性。

1　材料与方法

(1) SBR 反应器(见图 1):直径 20 cm,高 60 cm,总容积 12 L。内装有 DO 探头,曝气砂头,外接溶氧仪,电磁式空气压缩机,气体流量计。

(2) 试验污水:北京某制药厂生产废水。废水成分见表 1。

(3) 试验污泥:经制药废水长期驯化的活性污泥。

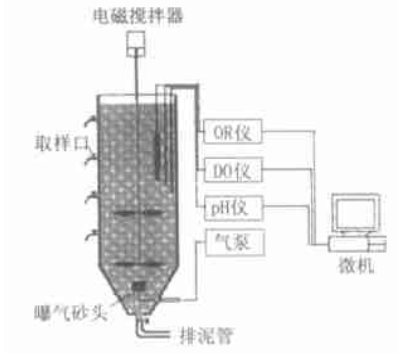

图 1　SBR 反应器示意

表 1　试　验　废　水　成　分

COD/ mg/ L	pH	NH_3 - N/ mg/ L	NO_2^- - N/ mg/ L	NO_3^- - N/ mg/ L
1 224	9.7	127	0.6	0.8

(4) DO,pH 使用仪器在线测定,COD 根据 DO 变化取样,样品用 COD - 571 - 1 型消解装置消解。

2　结果与讨论

2.1　制药废水试验

2.1.1　有预曝气的反应

预曝气:指在 SBR 反应器进水之前,对上次反应残液与活性污泥的混合液曝气大约 5 min。

试验为瞬时进水。通过气体流量计控制曝气量恒定。DO 仪在线监测,每分钟记录读数一次。根据 DO 变化情况,取水样,并测定 COD。

试验结果见图 2。反应进行到 15～30 min 时,COD,DO 曲线上都出现了偏离变化规律的一段,而

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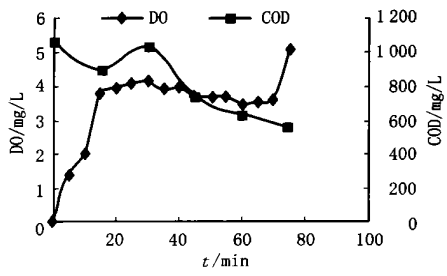

图 2　制药废水有预曝气时结果

且 DO 曲线在 30 min 后还有异常的周期性波动。

对于 COD 曲线,COD 应该随时间逐渐下降,但随着反应的进行,COD 下降的速率会减慢,表现为曲线斜率减小。图 2 中 COD 在前 15 min 正常下降,但在紧接的 15 min 内却逐渐上升,并在 30 min 时达到另一个峰值,之后才正常下降。对于 DO 曲线,前 15 min 上升,是曝气的复氧速率大于活性污泥的耗氧速率。因为污泥处于闲置期后的恢复状态,且活性污泥在 DO 水平较低时首先对水中有机物进行吸附,此时耗氧速率低。按照正常规律,活性污泥对有机物吸附饱和后进行新陈代谢降解,耗氧速率随之增长,并大于复氧速率,因此 DO 应该在随后的反应中缓慢下降,直至 COD 降解接近结束,DO 出现陡升。但是 DO 却在 15～30 min 这段时间内出现了异常的上升并达到峰值,恰好与 COD 曲线的异常一致。

分析原因,COD 与 DO 曲线在 15～30 min 之间的异常应该是:活性污泥微生物在进水前的预曝气阶段进行内源呼吸,处于饥饿状态,即被活化。活化后的污泥对底物的吸附增强。然而,对于有毒制药废水,微生物吸附作用越强,所受毒性冲击也越大,并且瞬时进水更加强了毒性,这样微生物就会自发地解吸,以降低毒性。在解吸过程中,微生物通过新陈代谢作用,将底物无毒化,然后在解吸结束时进行正常的生物降解。解吸时耗氧速率小于复氧速率,DO 曲线上升;降解时耗氧速率大于复氧速率,DO 曲线下降。30 min 后 DO 的波动则是无毒化与降解过程的交替,因为 COD 曲线无异常;DO 曲线的最后陡升,则表示易降解物质的降解接近结束。

为了验证以上推论,设计了试验 2.1.2。

2.1.2　无预曝气的反应

在进水前不曝气,直接瞬时进水。通过气体流量计控制试验曝气量同 2.1.1,DO,COD 的读取与测量也同上。试验结果见图 3。

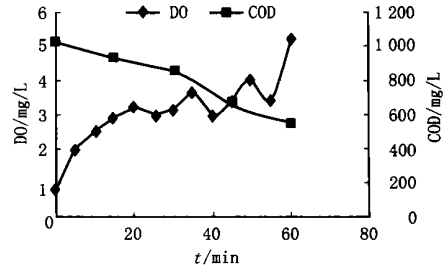

图 3　制药废水无预曝气时结果

由图 3 可知,虽然是同样的制药废水,但在无预曝气的情况下,COD 曲线没有出现明显的异常,只是 DO 曲线在 20 min 后有波动,且波动幅度比有预曝气时大。COD 无明显异常说明微生物中毒不深,因此当污水有毒时,应该避免预曝气,还可以通过延长进水时间与非限量曝气来缓解毒性对活性污泥的抑制。对于 DO 曲线的波动解释同上,是无毒化与降解过程的交替。对于波动比有预曝气时大解释为:由于无预曝气反应没有经历有预曝气反应的强吸附、强毒性冲击,所以生物活性受抑制小,解毒能力强,相应的无毒化与降解周期都延长了。

虽然试验 2.1.2 验证了上述解释的正确性,我们还是设计了如下试验以保证结论的严谨。

2.2　生活污水试验

试验用水为生活污水。曝气控制、DO 读数、COD 取样测定都同试验 2.1。分别做了有、无预曝气两组平行试验。试验结果见图 4,图 5。

从图 4 和图 5 中可以看到两种情况都符合正常规律,再次充分说明了 DO 曲线的异常是由制药废水毒性引起的。值得注意的是:生活污水浓度低,反

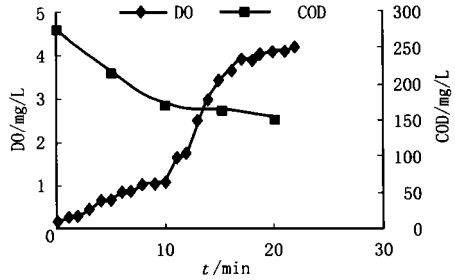

图 4　生活污水无预曝气结果

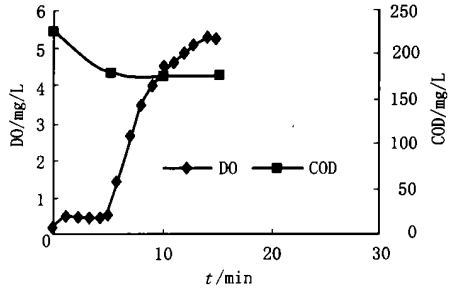

图 5　生活污水有预曝气结果

应时间短,通过 DO 判断终点时本文采取了延时曝气,所以 DO 曲线较制药废水而言,陡升段长,还多了一段平台。

2.3　曝气方式与曝气量的影响

图 6 显示的所有试验方案的 DO 曲线中,只有制药废水在无预曝气运行的条件下,DO 曲线才表现出明显的周期性的波动。

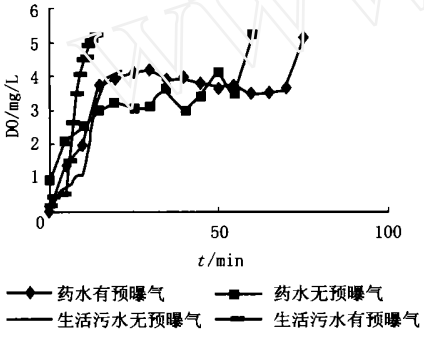

图 6　DO 变化判断制药废水毒性

因此,建议对于一种待定毒性的制药废水,可以做三组平行试验:有预曝气、无预曝气、非限量曝气的运行,并监测 DO 变化,同时联机绘制 DO 曲线,任意一条 DO 曲线出现异常的周期性波动,都可判断此水样有毒。依有预曝气、无预曝气、非限量曝气的顺序,DO 周期性波动出现得越靠后,说明水样毒性越强,反之水样毒性较弱。

同时值得注意的是:曝气量过大导致的 DO 过高将影响制药废水毒性的判断。由图 7 知 COD 曲线已表现出明显的解吸与降解的交替,但 DO 曲线却是正常的。较大的 DO 说明未被利用的氧气量过大,那么即使在解吸时耗氧速率的减小使得 DO 上升,上升的部分相对于系统的原有 DO 来说也是微小的,不足以产生明显的DO跃升,因此影响以DO

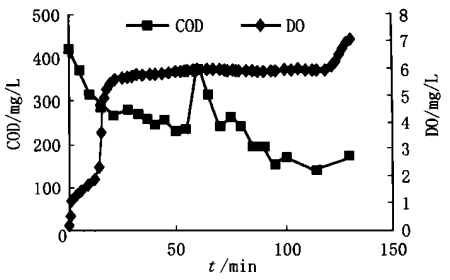

图 7　DO 过大影响毒性判断

作为标志判断制药废水的毒性。

3　结语

(1) 药品性能要求药物对生物作用的微量高效性,DO 可灵敏反应微生物的活性,这两者奠定了 DO 在线监测判断制药废水毒性的理论依据。

(2) 在制药废水与生活污水的平行试验中,无毒的生活污水的 DO 曲线符合常规变化,有毒的制药废水的 DO 曲线出现了特有的周期性波动,据此证明了(1)的理论,并找到了在线监测判断制药废水毒性的 DO 特征曲线。

(3) DO 曲线的周期性波动解释为活性污泥微生物对底物无毒化与解降的周期性交替,此为微生物对外界刺激的一种应激反应。微生物将底物无毒化,以改善生物的生存环境并得到降解时可同化的营养来维持生存。无毒化时耗氧速率小于复氧速率,DO 曲线上升,降解过程耗氧速率大于复氧速率,DO 曲线下降。

(4) 为得到最易辨识的特征 DO 曲线,可采用不同的曝气方式和曝气量,以加强、减弱水样毒性对微生物的冲击,使微生物总有一个活性状态能反应 DO 特征周期波动。同时还应注意试验中 DO 不能过高。

参考文献

1　沈耀良,等. 废水生物处理新技术理论与应用. 第一版. 北京:中国环境科学出版社,1999

▲作者通讯处:100022 北京市朝阳区建国路 88 号 sohu 现代城 B 座 1109 室 北京华利嘉环境工程技术有限公司
电话:(010) 85802596
E-mail:fancaicai1000 @sohu.com
收稿日期:2002-11-29

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ABSTRACTS

Abstract: This project of wastewater reuse includes the dredging of Minxin River and reconstruction of Qiaoxi Wastewater Treatment Plant in the capital city of Hebei Province, it is expected to provide water for environmental, industrial and domestic purposes. The existing secondary treatment was enhanced by well-chosen advanced tertiary treatment with sophisticated process, which is reliable, stable, easy to operate and highly automatic. Also it is low in expenses and flexible in operation. Enough good results have been obtained.

Abstract: By series discussions on feasibility and economical and technical analysis the author believed that so called dual water supply, separate delivery for drinking and miscellaneous consumptions was inconsequential both in technical and economical sides. Also it is impracticable in engineering arrangement and a lot of difficulties in management will be aroused. Best way of improvement might be laid on full quality upgrading of urban water supply on basis of technical advancement.

Abstract: On the basis of the operating records of Jiuxianqiao WWTP (March to October 2001) and Fangzhuang WWTP (January to June 2001) in Beijing, problems related to the surplus sludge volume calculation in activated sludge process are investigated. Correlation between sludge yield index (SYI) and MLVSS/MLSS ratio has established, and by this correlation the causes of large-range fluctuation of SYI are discussed.

Abstract: The pollutants in the Baishi reservoir which is under construction are forecasted by dynamic simulation for a hydrological and meteorological year round. The result shows that there is self-purification capacity to pollutants in the reservoir and it is stable, and slightly affected by the run off, water quality and temperature. If no additional pollution inputs, when the equilibrium of impounding to the dam is established, most water quality indicators of the mass of the reservoir will meet the target of class Ⅲ in the national surface water standard or better, except that the indicators of LAS and oil will be within class Ⅳ and total nitrogen in class V. Therefore the wastewater treatment and inputs into the basin must be controlled strictly.

Abstract: Corrosion inhibition, scale retardation, sterilization and algae control play very important roles for water quality stabilization in circulating cooling water system of air condition facilities in industry and buildings. In this paper chemical formulations of composite basic agents, including scale retarder, dispersant, corrosion inhibitor and germ/algaecide are presented and dosage calculation, dosing method and location and other attentions deal with the application of these chemicals are given. Furthermore the importance and operation of external filtration and pre-membrane growth for systematic clearing are presented briefly.

Abstract: On the basis of experimental research on the competition between sulfate reducing bacteria and methane producing bacteria, the effect of sulfate reduction product on the process and the operating performances of the reactor, it is affirmed that both the single-phase UASB or composite anaerobic reactor are feasible to treat sulfate contained organic wastewater. But rather low COD removal than for the non-sulfate containing wastewater. Anaerobic filter can be employed as reactor of sulfate-reduction-phase in the two-phase anaerobic digestion process.

Abstract: Parallel experiments of SBRs feeded with pharmaceutical wastewater (PW) and domestic wastewater (DW) respectively were done, and the reactors were operated either with or without pre-aeration. The DO curve of DW was routine, while that of PW showed proper periodic fluctuant. The DO level in the reactor was monitored on-line and COD sample was examined on time for control. It was believed that the toxicity of the raw PW could be looked by the on-line DO monitoring data qualitatively. The periodic DO fluctuant could be recognized as the periodic alternation of desorption and degradation of bentho-substances by organisms in activated sludge. The most PW toxicity identifying DO curve has been obtained in further experiments. The impacts of the raw toxic wastewater on the microorganisms shall be increased, balanced or decreased in cases of non-pre-aeration, pre-aeration and unlimited pre-aeration respectively. In case of over-aeration the DO fluctuant will be covered up by the high DO level in the reactor.