

混合基质条件下难降解有机物生物降解性能*

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摘要 选取几种典型的难降解杂环化合物, 在混合基质条件下较为系统地研究了其好氧生物降解性能以及难降解有机物间的联合作用效果. 研究表明, 吡啶、喹啉与其同系物具有类似的生化降解过程及抑制机理, 它们的联合作用效果为相加作用; 具有不可逆抑制作用物质共存时联合作用效果为协同作用; 具有不可逆抑制作用物质与可逆抑制作用物质共存时, 联合作用效果为拮抗作用.

关键词 难降解有机物, 生物降解性能, 联合作用, 混合基质, 杂环化合物.

实际工程中含有难降解有机物的工业废水是多种成分共存的混合液. 目前, 有关有机物生物降解性能的研究大多采用单一基质水质和单一菌群条件. 因此, 所得的研究结果与实际废水处理情况相比有一定差距, 难以有效地指导工程实践. 本研究选取几种典型的难降解杂环化合物, 在混合基质条件下研究其好氧生物降解性能以及难降解有机物间的联合作用效果.

1 试验材料和方法

本研究采用瓦呼仪测试方法, 水样配制:

(1) 苯酚单基质水样 苯酚是含杂环化合物废水中含量高、降解性能较好的一种典型物质, 选用它作为受试物生物降解性能评价的参照物质.

- (2) 1种受试物与苯酚组成共基质水样.
- (3) 2种受试物与苯酚组成混合3基质水样.
- 接种污泥采用某焦化厂活性污泥法曝气池中的活性污泥. 试验所选受试物及测试浓度如表1所示.

2 试验结果与讨论

2.1 难降解有机物与其同系物

以吡啶为例, 试验中分别选取甲基吡啶和氰基吡啶与吡啶组成混合基质水样. 图1和图2分别为甲基吡啶和氰基吡啶在不同基质条件

表1 受试有机物及测试初始浓度 ¹⁾ /mg·L ⁻¹			
受试物	测试浓度	受试物	测试浓度
吡 啶	40	喹 啉	60
甲基吡啶	40	异喹啉	60
氰基吡啶	40	呋 啉	30
咪 唑	40	联 苯	30

1) 在用苯酚作共基质试验时, 反应瓶内苯酚的初始浓度为50mg/L.

下的瓦呼仪曲线. 可以看出:

(1) 甲基吡啶、氰基吡啶与吡啶降解性能类似, 在浓度为40mg/L 时, 相对累积耗氧量曲线均低于单一基质苯酚的耗氧量曲线, 对苯酚的降解产生了明显的抑制作用, 它们的抑制率见表2, 3者的抑制性顺序是氰基吡啶> 甲基吡啶> 吡啶.

(2) 在混合3基质条件下, 3种物质组成混合水样的相对耗氧量曲线低于苯酚单基质及它与其中一种物质的共基质曲线, 对苯酚降解的抑制作用进一步加重, 在表2中列出了混合3基质的抑制率.

(3) 分析表2中数据发现: 混合3基质条件下, 对苯酚的抑制率约为难降解有机物分别与苯酚组成共基质时抑制率之和(如氰基吡啶的抑制率13.78%与吡啶的抑制率9.74%之和近

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表2 甲基吡啶及氰基吡啶在共基质及3基质条件下对苯酚降解的抑制率/%

同系物为氰基吡啶			同系物为甲基吡啶		
吡啶+ 苯酚	氰基吡啶+ 苯酚	吡啶+ 氰基吡啶+ 苯酚	吡啶+ 苯酚	甲基吡啶+ 苯酚	吡啶+ 甲基吡啶+ 苯酚
9. 74	13. 78	23. 96	9. 74	11. 15	21. 09

似于混合3基质的抑制率23. 97%) ,可见吡啶与其同系物之间联合作用效果为相加作用.

吡啶与其同系物化学结构相近,在微生物体内的生物代谢过程类似.从图1及图2甲基吡啶、氰基吡啶的瓦呼仪测试曲线可见,在很低浓度时,它们对苯酚降解产生持续抑制作用,随着时间的延长,抑制作用始终没能解除,因此它们对微生物的抑制机理同吡啶一样,都属于不可逆抑制范畴.由此可见,吡啶与其同系物具有相同或类似的生化降解过程及抑制机理,它们的联合作用效果为相加作用.

同样,在喹啉与其同系物异喹啉生物降解性能的研究时得到相同的结论,即喹啉与其同系物异喹啉具有类似的生化降解过程,并且它们的抑制机理均属可逆抑制范畴,联合作用效果为相加作用.

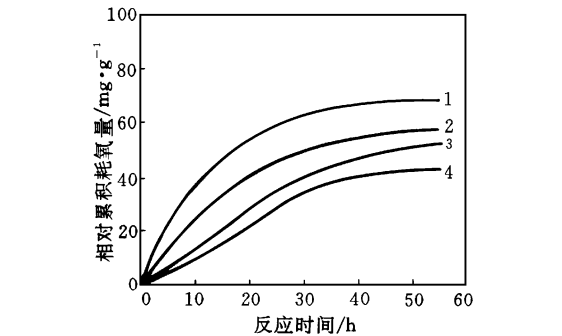


图1 吡啶、甲基吡啶在共基质及混合3基质条件下相对累积耗氧量

1. 苯酚单基质(50mg/L) 2. 苯酚(50mg/L) + 吡啶(40mg/L)
3. 苯酚(50mg/L) + 甲基吡啶(40mg/L)
4. 苯酚(50mg/L) + 吡啶(40mg/L) + 甲基吡啶(40mg/L)

2. 2 非同系有机物

2. 2. 1 吡啶与咪唑、联苯

选取了吡啶及与其生物降解性能类似的有机物咪唑和联苯与苯酚组成混合3基质.图3和图4分别为咪唑、联苯、吡啶在不同基质条件下的瓦呼仪曲线.可以看出:

(1) 吡啶和咪唑、联苯与苯酚共基质时均产生了严重的不可逆抑制效果.当它们分别与苯

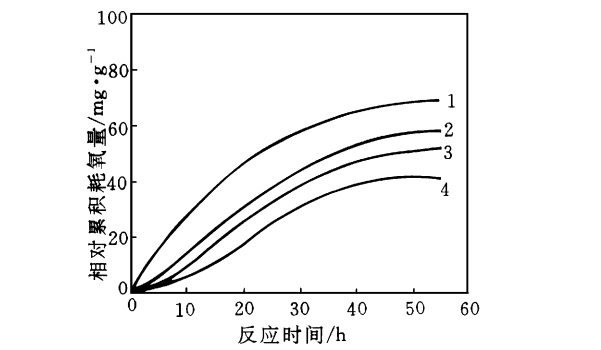


图2 吡啶、氰基吡啶在共基质及混合3基质条件下相对累积耗氧量

1. 苯酚单基质(50mg/L) 2. 苯酚(50mg/L) + 吡啶(40mg/L)
3. 苯酚(50mg/L) + 氰基吡啶(40mg/L)
4. 苯酚(50mg/L) + 吡啶(40mg/L) + 氰基吡啶(40mg/L)

酚组成混合3基质时,抑制作用急剧增加,3基质的相对累积耗氧量曲线远远低于苯酚单基质及吡啶、咪唑、联苯单独与苯酚的共基质曲线.表3为不同基质条件下对苯酚降解的抑制率.

(2) 3基质的抑制率远远大于各物质单独与苯酚共基质时的抑制率之和(43. 7> 9. 74+ 28. 4; 42. 2> 9. 74+ 21. 5).因此,可以认为吡啶、联苯、咪唑这3种物质的联合作用效果为‘协同作用’^[2].在生物处理中应避免这类物质共存.

(3) 上述物质均为不可逆抑制物质,它们对酶活性的抑制使酶发生了难以再生修复的化学性损伤,当这类物质共存时,势必会加剧酶的损伤,使酶活性严重降低,从而使其生物降解性能大大下降.

2. 2. 2 吡啶与喹啉

图5为吡啶、喹啉在不同基质条件下的瓦呼仪曲线.混合3基质的相对累积耗氧量曲线在降解初期介于喹啉与吡啶单独共基质的耗氧量曲线之间,之后降解性能逐渐得以恢复,至55h时,3基质的相对累积耗氧量高于喹啉共基质时的累积耗氧量,不仅吡啶对苯酚的抑制作用解除了,而且吡啶也得到一定程度的降解.

表3 咪唑、联苯在不同基质条件下的抑制率

物质	吡啶+ 苯酚	咪唑+ 苯酚	吡啶+ 咪唑+ 苯酚	吡啶+ 苯酚	联苯+ 苯酚	吡啶+ 联苯+ 苯酚
抑制率/%	9.74	28.4	43.7	9.74	21.5	42.2

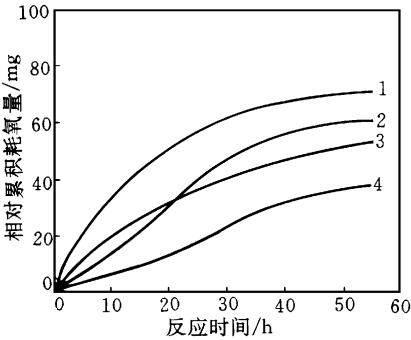


图3 吡啶、咪唑在共基质及混合3基质条件下相对累积耗氧量

1. 苯酚单基质(50mg/L) 2. 苯酚(50mg/L) + 吡啶(40mg/L)
3. 苯酚(50mg/L) + 咪唑(30mg/L)
4. 苯酚(50mg/L) + 吡啶(40mg/L) + 咪唑(30mg/L)

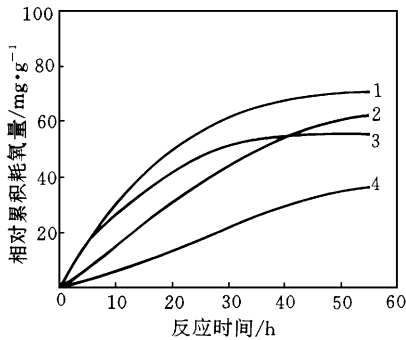


图4 吡啶、联苯在共基质及混合三基质下相对累积耗氧量

1. 苯酚单基质(50mg/L) 2. 苯酚(50mg/L) + 吡啶(40mg/L)
3. 苯酚(50mg/L) + 联苯(30mg/L)
4. 苯酚(50mg/L) + 吡啶(40mg/L) + 联苯(30mg/L)

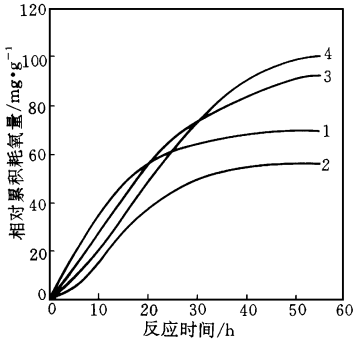


图5 吡啶、咪唑在不同基质条件下的相对累积耗氧量

1. 苯酚单基质(50mg/L) 2. 苯酚(50mg/L) + 吡啶(40mg/L)
3. 苯酚(50mg/L) + 咪唑(60mg/L)
4. 苯酚(50mg/L) + 吡啶(40mg/L) + 咪唑(60mg/L)

对上述试验现象可做如下解释: 在受试浓度下, 吡啶与苯酚共基质时是严重且持续抑制苯酚降解的, 但当咪唑与它共存时, 由于咪唑对微生物产生可逆抑制, 呈现先抑制、后诱导的特点, 随着咪唑诱导期的出现, 多功能氧化酶体系由于诱导作用使其总量增加, 从而加速了咪唑的降解, 同时也抵消了吡啶对微生物的抑制作用, 使吡啶有一定程度的降解. 因此, 咪唑与吡啶之间具有明显的拮抗作用, 即咪唑的存在对吡啶的降解具有消除抑制、促进降解的作用.

同样, 咪唑和联苯具有与上述完全类似的降解性能及联合作用效果. 咪唑与联苯之间具有明显的拮抗作用, 咪唑为联苯较有效的拮抗剂.

3 结论

(1) 吡啶及其同系物或咪唑及其同系物在与苯酚组成混合基质时, 由于吡啶和咪唑与它们同系物具有相同的生化降解过程, 它们之间联合作用效果为相加作用.

(2) 不可逆抑制作用物质(如吡啶、咪唑、联苯)共存时联合作用效果为协同作用, 其共存将加剧物质的难降解性及对微生物的抑制性.

(3) 不可逆抑制作用物质与可逆抑制作用物质共存时, 联合作用效果为拮抗作用(如吡啶与咪唑; 咪唑与联苯). 咪唑和咪唑的存在将减弱吡啶、联苯的抑制性, 提高其降解性能.

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Key words: Lake East Tahu, aquatic plants, silting-up, phosphorous.

Study on Characteristics of Organics in the Eutrophic Source Water of Shaoxing City.

Xiaohong Luo, Lili Cao, Zhansheng Wang (Dept. of Environ. Eng., Tsinghua University, 100084): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 13_16

Ultrafiltration was used in this study to determine the organics molecular weight(MW) distribution in the eutrophic source water of Shaoxing City. The deviation to color and UV 254 of organics in each MW range was also investigated. Then the characteristics of organics in the three typical source water (Huai River, Miyun Reservoir and Shaoxing's eutrophic lake) were compared. It was found that the characteristics of organics in the water relate closely to its source. Organics in Miyun Reservoir are mainly of low MW, with $MW < 3000$ occupying 96.7%, while organics in Shaoxing source water and Huai River cover a more wide MW range, organics with $MW > 3000$ in the source water is 28.37% and 38.28% respectively.

Key words: organic, MW, SUVA, eutrophic.

The Preparation and Characterization of a New Kind of Inorganic Polymer Flocculant— Ferric Polysilicate (FPS). Wang Dongsheng, Wu Qifang, Wei Chaohai (Department of Applied Chemistry, SCUT, Guangzhou 510641): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 17_19

A new kind of inorganic polymer flocculant — Ferric Polysilicate (FPS) was prepared by using water glass, ferric chloride and inorganic acid as material. Several factors of preparation were discussed. The experimental results showed that FPS was best prepared at Fe/Si ratio of 1 and activation time of one hour. Compared with PFC, FPS showed better capability of turbidity removal.

Key words: inorganic polymer flocculant, activated silica, ferric chloride, coagulation mechanism.

Study on Biodegradability of Refractory Organics Under the Condition of Mixed Substrates. He Miao, Zhang Xiaojian et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 20—22

A systematic study was conducted on the biodegradability and the co-effect of refractory organics for several typical refractory heterocyclic compounds under the condition of mixed substrate. The experimental results showed that pyridine, quinoline and homologous compound have similar biodegradation and inhibitory mechanism, of which co-effect shows

additive one; while the co-effect of the irreversible inhibitory substrates shows a cooperative effect, the co-effect of irreversible mixed with reversible inhibitory substrates shows a contradictory effect.

Key words: refractory organics, biodegradability, co-effect, heterocyclic compounds, mixed substrate.

Pollution of Nitrogen and Phosphorus in the Region of Wastewater Irrigation along Kui River.

Jiang Cuiling, Xia Ziqiang and Liu Ling (Dept. of Hydrology and Water Resources, Hecai Univ., Nanjing 210098), Wang Lei and Wan Zhengcheng (Xuzhou Hydrology and Water Resources Survey Section, Xuzhou 221006): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 23_25

Simulated test of wastewater irrigation in the field and chemical analysis of nitrogen and phosphorus in the soil and groundwater at wastewater irrigation area and control area showed that high contents of nitrogen and phosphorus in the wastewater had markedly improved soil fertility and the crop in irrigation area grew very well, but nitrogen and phosphorus which could pollute surface and ground water were accumulated in the soil. Ammonium ion was easily intercepted, sorbed and transformed by soil, but high concentration of ammonium ion could slowly transport downward and accumulate in upper levels of phreatic water. Wastewater irrigation and rainfall drip can wash nitrite and nitrate ions produced by nitrification in the soil and pollute groundwater. The contents of nitrite and nitrate ions in shallow groundwater were still seriously beyond standard at condition of saturating irrigation after experience of three months.

Key words: nitrogen, phosphorus, wastewater irrigation, Kui River Area.

Study of the Effect of Simulated Acid Rain on the Physical and Chemical Properties of Main Soil Types in Shandong Province. Xiao Yuefang, Shi Yanxi, Liu Chunsheng et al. (College of Resources and Environment, Shandong Agricultural University, Taian 271018), Song Guohan (Institute of Soil and Fertilizer, Shandong Provincial Academy of Agricultural Science, Jinan 250100): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 26_29

Five types of soils i. e. brown earth, cinnamon soil, chao soil (cultivated fluviogenic soil), lime concretion black soil, salt-affected soil were leached by earth volume test with simulated acid rain of which the value of pH are 2, 3, 4, 5, separately from one year to ten years. The results showed that the pH values of the leached four soil types which had been