焦化废水中有机物曝气吹脱条件下的挥发特征*

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摘要 焦化废水中各类有机物表现出不同的挥发特征. 乙苯、萘等11种物质比较容易挥发, 12h 空曝后其去除率约为20% —40%, 它们的挥发速率常数 K_V 与 Henry 常数间具有良好的线性相关关系, 线性相关方程为 $K_V = 2.906 \times 10^3 H + 0.0146$, 挥发作用在这类物质的去除中起着重要作用; 苯酚等12种物质具有中等程度的挥发性; 间苯二酚等物质其挥发作用不明显.

关键词 挥发特征, 焦化废水, 空曝试验, 曝气吹脱, 挥发性有机物, 速率常数.

在传统的活性污泥法曝气池中, 曝气作用可部分吹脱废水中挥发性污的有机物, 尤其对于强挥发性的有机物来说, 由曝气吹脱可使挥发性染物不经微生物分解而直接从水中逸入大气, 造成了处理厂附近的空气污染. 对此, 挥发性有机物的曝气吹脱问题已成为国内外广泛关注的问题. 焦化废水是含挥发性污染物较多的一种废水, 本研究将对废水中各类有机物在曝气吹脱条件下的挥发特性进行研究.

1 试验方法

采用空曝试验法. 试验装置为完全混合式曝气池, 试验用水采用首钢焦化厂的曝气池进水. 曝气池内不投加活性污泥, 其余各种运行条件与实际焦化厂处理装置安全一致. 试验过程中定时从曝气池中取样进行 TOC 及 GC/MS 分析.

2 曝气吹脱对废水中各类有机物的去除

表1为经不同空曝时间后废水的 TOC 测定结果.

表1 空曝试验 TOC 测定结果

项目	空曝时间/h				
	0	6	12	24	48
TOC/mg·L^{-1}	316.0	294.5	289.7	268.6	262.2
去除率/%		6.8	9.1	15.0	17.0

由表1可见, 曝气可吹脱废水中的部分有机物, 使总的 TOC 下降, 当空曝时间为12h 时, TOC 的去除率为9.1%, 当空曝时间延至24h 时, TOC 的去除率达15%, 所以曝气吹脱对于有机物的去除起着一定的作用. 为了进一步了解曝气吹脱对焦化废水中各种有机物的吹脱效果, 针对焦化废水中所含的24种有机物进行曝气吹脱实验. 测定不同曝气时间下的 TOC 变化情况, 将实验数据进行整理分析, 焦化废水中有机物按挥发特性大致可分为以下3类.

(1) 挥发性较强, 曝气吹脱作用较为明显的有机物. 这类物质于不同空曝时间下 TOC 浓度变化列于表2.

从表2可知, 这类物质因曝气挥发作用引起的去除很明显, 在经过12h 空曝后它们的 TOC 去除率约20% —40%, 因此, 可以认为这11种物质是易挥发性的, 在生物处理过程中曝气对物质去除起着很重要的作用, 因此在进行生物降解特征的研究中必须充分考虑由于挥发而引起的去除量, 以免产生很大的误差.

(2) 中等程度挥发有机物. 这类物质不同空曝时间下 TOC 浓度变化见表3.

表3中的物质在曝气吹脱作用下有一定程度的挥发, 但 TOC 浓度下降幅度不大, 经12h

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表2 不同空曝时间条件下强挥发的有机物 TOC 浓度变化/mg·L⁻¹

物质	原水	6h 空曝		12h 空曝		24h 空曝		48h 空曝	
		TOC	去除率/%	TOC	去除率/%	TOC	去除率/%	TOC	去除率/%
乙苯	18.23	14.52	20.4	12.14	33.4	8.815	51.6	5.247	71.3
甲苯	7.015	5.755	18.0	4.721	32.7	3.10	52.8	2.309	67.0
二甲苯	4.993	4.196	16.0	3.552	28.9	2.895	42.0	1.740	65.1
呋喃	2.054	1.765	14.0	1.443	30.2	1.21	41.9	0.789	61.5
萘	3.318	2.978	10.5	2.673	19.4	2.154	35.1	1.983	40.2
吡啶	3.982	3.270	17.9	2.816	29.2	2.019	49.3	1.782	55.2
甲基吡啶	0.442	0.360	18.6	0.294	33.5	0.247	44.1	0.208	52.9
C_4烷基吡啶	0.79	0.640	18.9	0.52	34.1	0.410	48.1	0.330	58.2
C_2烷基吡啶	0.569	0.467	17.9	0.383	32.7	0.284	50.0	0.215	62.2
吡咯	3.886	3.006	12.6	2.365	39.1	1.719	55.8	1.001	74.2
联苯	3.697	3.298	11.0	2.943	20.4	2.343	36.6	1.854	49.9

表3 不同空曝时间条件下中等程度挥发有机物 TOC 浓度的变化/mg·L⁻¹

物质	原水	6h 空曝		12h 空曝		24h 空曝		48h 空曝	
		TOC	去除率/%	TOC	去除率/%	TOC	除率/%	TOC	去除率/%
苯酚	94.07	89.27	5.11	86.8	7.72	83.21	11.5	80.90	14.0
甲基苯酚	42.34	41.18	2.73	39.95	5.64	37.21	12.1	36.87	12.9
二甲苯	28.53	27.75	2.38	26.91	5.68	25.91	9.5	24.92	12.6
2,3,5-三甲基苯酚	6.415	6.22	3.04	6.01	6.31	5.72	10.8	5.35	13.5
喹啉	16.62	15.99	3.79	15.34	7.7	14.51	12.7	13.98	15.9
异喹啉	8.318	8.02	3.58	7.60	8.63	6.99	15.9	6.42	20.4
甲基喹啉	9.227	8.82	4.40	8.41	8.85	7.86	14.8	7.21	20.8
吲哚	3.602	3.412	5.27	3.305	8.25	3.007	15.6	2.915	19.0
苯并呋喃	2.338	2.251	3.72	2.174	7.01	2.005	14.2	1.982	15.2
苯并噻吩	1.706	1.635	4.16	1.586	7.02	1.450	15.00	1.33	22.0
苯并咪唑	2.244	2.15	4.18	2.09	7.75	1.95	13.1	1.89	15.7
蒽	3.097	2.94	5.06	2.86	7.65	2.72	12.2	2.54	17.9

的空曝后, 其 TOC 去除率在 5.64%—8.985%, 挥发不如第一类物质明显.

(3) 弱挥发或难挥发有机物 这类物质以间苯二酚为代表, 经过空曝后, TOC 浓度几乎没有变化, 挥发作用对有机物去除效果的影响可忽略不计.

3 焦化废水中有机物的挥发特征

Mackay、Wolkoff、Liss、Smith 等人根据界面双膜等理论, 在研究热力学和动力平衡基础上分析了物质的挥发过程, 提出了多种描述物质挥发特性关系式[2], 其中 Mackay 和 Wolkoff 提出的关系式是在充分混合的水体中建立的, 比较接近废水生物处理曝气池中的水力特点.

$$c = c_0 \cdot e^{-K_V t} \quad (1)$$

式中, c: 经 t 时后水中的物质浓度(mg/L); c_0: 水中物质的初始浓度(mg/L); t: 挥发时间(d); K_V: 挥发速率常数(d^{-1}).

表4列出了利用式(1)对于一些强挥发物质及中等程度挥发物质算出的挥发常数, 同时还

列出了各物质的 Henry 定律常数.

表4 有机物挥发速率常数与 Henry 定律常数

挥发程度	物质名称	挥发速率常数/ d^{-1}	Henry 定律常数[3] / $atm \cdot m^3 \cdot mol^{-1}$
强挥发物质	乙苯	0.041	8.7×10^{3}
	甲苯	0.029	6.6×10^{3}
	二甲苯	0.027	5.1×10^{3}
	呋喃	0.030	5.4×10^{3}
	萘	0.018	1.15×10^{3}
	吡啶	0.035	7.0×10^{3}
	吡咯	0.045	9.3×10^{3}
	联苯	0.019	1.5×10^{3}
中等程度挥发物质	苯酚	8.36×10^{-4}	3.97×10^{-7}
	甲基苯酚	9.87×10^{-4}	2.16×10^{-6}
	二甲基苯酚	8.54×10^{-4}	$< 1\times10^{-6}$
	吲哚	9.43×10^{-4}	$< 1\times10^{-6}$
	喹啉	9.79×10^{-4}	9.35×10^{-7}
	异喹啉	9.21×10^{-4}	9.86×10^{-7}

从表4可知:

(1) 不同挥发程度的物质其挥发速率常数 K_v 差别很大, 在0.018—045d^{-1}之间, 而中等程度挥发物质与强挥发物质 K_v 值相差2个数量级.

(2) 在本研究中易挥发物质的挥发速率常数 K_v 与 Henry 常数之间具有良好的线性相关关系, 对它们进行线性分析, 得如下方程:

$$K_v = 2.906\times10^{3}H + 0.0146 \quad (2)$$

($r = 0.987$)

式中, K_v: 挥发速率常数(d^{-1}); H: Henry 定律常数($atm \cdot m^3 \cdot mol^{-1}$).

4 结论

(1) 对焦化废水中24种有机物质进行空曝试验, 在曝气吹脱条件下, 各种有机物表现出不同的挥发特性.

(2) 有11种有机物, 包括乙苯、苯、吡咯、联苯等比较容易挥发, 它们的挥发速率常数 K_v 与 Henry 常数间具有良好的线性关系, 线性相关方程为 $K_v = 2.906\times10^{-3}H + 0.0146$, 挥发作用在有机物的去除中起很重要的作用.

(3) 苯酚、喹林等12种物质具有中等程度的挥发性; 间苯二酚在曝气吹脱条件下几乎不挥发.

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和释放受阻, 部分藻胞巨大且形状不规则. 和2, 4-二硝基甲苯等硝基芳烃类化合物对斜生栅列藻单一毒性[2]相比, 混合毒物在较高浓度下不仅阻碍斜生栅列藻的繁殖, 而且改变藻胞的形状.

(3) 当藻类生长阻碍率为45%—50%时, 混合毒物使斜生栅列藻部分藻胞的细胞核和细胞器解体, 这与2, 4-二硝基甲苯对斜生栅列藻单一毒性相比, 混合毒物的初始浓度均低于2, 4-二硝基甲苯的初始浓度. 且呈协同作用的混合毒性物的视野中, 斜生栅列藻呈现此中毒症状的藻胞占45%—50%; 呈拮抗作用的混合毒物视野中, 呈现此中毒症状的藻胞占30%左右. 可见混合毒性效应比单一毒性效应更为复杂.

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troaromatic compounds in the ecosystem, the study on the mixtoxicity of 2, 4-DNT and other 6 kinds of nitroaromatics to the algae (*Scenedesmus obliquus*) was carried out. 48h-EC_{50} of monotoxicity of 7 kinds of compunds and 48h-EC_{50} of mixtoxicity of 2, 4-DNT + 6 kinds of compounds were measured. Results indicated that there are synergisms between, 2, 4-DNT + 4-NAn, 2, 4-DNT + 4-NAnis, and 2, 4-DNT + 1, 4-DNB as well as antagonisms between 2, 4-DNT + 4-NT, 2, 4-DNT + 4-NPh and 2, 4-DNT + 4-NCB. Under the microscope (400 times) 3 kinds of toxic symptoms, the inhibition to the filial spores forming and releasing, the irregular big cells appearing, nucleus and cell organs as well as the protoplast distegrating were observed.

Key words: mixtoxicity, 2, 4-DNT, nitroaromatic compounds, algae, *Scenedesmus obliquus*.

Study on the Volatile Property of Organics in Coke-Plant Wastewater under the Aerated Stripping Condition. He Miao, Zhang Xiaojian etal. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 34—36

A study was conducted to determine the volatile property of organics in the coke-plant wastewater under the condition of aerated stripping. The results show that there are different volatile characteristics among the organics. 11 kinds of compounds such as ethylbenzene and naphthalene are more volatile. The removal rate can get to 20% - 40% after an aeration of 12 hours. Their volatile rate constant K_v have a fairly good linear relation with the Henry constant (H), of which relation equation is $K_v = 2.906 \times 10^3 H + 0.0146$. Volatile effect plays a very important role in the removal process of these organic compounds. 12 compounds like phenol have a medium volatile property. The other compounds like resorcinol have a low volatility.

Key words: volatile property, coke-plant wastewater, aerated stripping, volatile organic compound, volatile rate constant.

Activity, Kinetics and Spatial Variation of Dissolved Alkaline Phosphatase in Lake Donghu. Zhou Yiyong, Li Jianqiu, Chen Xudong et al. (Institute of Hydrobiology, The Chinese Academy of Sciences, Wuhan 430072): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 37—40

The extra cellular enzyme activities in aquatic environments are of monitoring significance. Dissolved alkaline phosphatase activities (APA_{Diss}) at the littoral outfalls, which receive the domestic waste water were significantly higher than those in pelagic zone in Donghu Lake. APA_{Diss} detected at the outfalls and in pelagic zone showed different relationships with soluble reactive phosphorus.

Key words: dissolved phosphatase, kinetics, characteristics, spatial distribution.

A Study on Bioaccumulation and Biomagnification of BHC and DDT in Baiyangdian Lake Foodweb. Dou Wei, Zhao Zhongxian (Institute of Zoology, Chinese Academy of Sciences, Beijing 100080): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 41—43

BHC、DDT and their metabolites were analysed in Duancun area from Baiyangdian Lake ecosystem in June 1995. The content levels of pesticides in water and bottom sediments were relatively lower: in water, the average values of BHC and DDT were 0.3μg/L and 0.1μg/L, respectively; in sediments, the residue level of BHC was same with DDT with a mean concentration of 0.7μg/kg(wet). The organochlorine insecticides content in aquatic organisms was much higher: the average concentration of BHC in hydrophytes, planktons, benthic macroinvertebrates, young-of-the-year *Carassius auratus and* 2-year-old *Ophiocephalus cris-pus* was 19.0, 30.0, 60.9, 17.2 and 110.7 μg/kg, respectively; for DDT, the content sequence was 6.3, 21.0, 37.9, 19.4 and 124.4g/kg, respectively. So the lipophilic nature and low biodegradation rates of BHC and DDT led to the accumulation of these compounds and subsequent magnification of concentration in organisms progressing up the food chain. DDT had a much profound bioaccumulation potential than BHC for the bioconcentration factor of DDT in organisms (63.3- 1244) was well above that of BHC (63- 369). The ratios of BHC isomers monitored in organisms ($\delta > \alpha > \gamma > \beta$) were different from that in water and sediments ($\alpha > \delta > \gamma > \beta$). The predominant DDT derivative was p, p′-DDE. Base upon the observed that the original DDT (P, P′-DDT) was indentified in some specimens, it has been concluded that there was a recent input of DDT to Baiyangdian Lake.

Key words: Baiyangdian Lake ecosystem, BHC, DDT, foodweb, the bioconcentration factor.

Joints Toxicities of Heavy Metals and Pesticides to *Pagrosomus major and Rhabdosargus sarba* Larvae. Dai Jiayin, Zheng Weiyun, Wang Shuhong (Environ. Sci. Res. Centre, Xiamen University, Xiamen 361005): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 44—46

The additive index of coeffects was used to study the toxicities of Cu-Mn, Cu-isofenphos-methyl and methamidphos-isofenphos-methyl