

用超滤技术评价絮凝法处理制浆废水 最佳 COD 去除效果的探讨

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摘要 利用超滤的分离特性剖析制浆洗漂废水及其絮凝上清液的 COD 的分子量分布, 以探讨、评价絮凝法处理此类废水所能达到的最佳 COD 去除效果。研究结果表明, 洗漂废水中 $MW > 10000$ 与 $MW < 3000$ 的物质是 COD 值的主要组成部分, 占 76%; COD 最佳去除效果为 71.3%。

关键词 超滤, 絮凝, 制浆废水。

絮凝物化法是水处理的基本方法之一, 具有工艺流程简单, 一次性投资少等特点。根据我国制浆造纸行业的特点, 絮凝物化法至今仍为治理污染危害的有效方法。

超滤(UF)作为一种技术与分离手段在食品、医药、分析、水处理等诸多领域均有应用。本试验利用其分离特性剖析制浆洗漂废水中 COD 的分子量分布, 以探讨、评价絮凝物化法处理此类废水所能达到的最好 COD 去除效果。

一、主要仪器、材料与试验方法

(一) 试验用主要仪器、材料

1. H-60 型超滤器(湖南省湘潭净化器厂)
2. 超滤膜(截留分子量 10000、3000, 中科院生态环境研究中心治理室)
3. 洗漂废水(碱法、H₂ 漂白草浆, 北京造纸七厂); 絮凝处理后洗漂废水(试验室自制)。

(二) 试验方法

选取截留分子量、10000、3000 的超滤膜, 对洗漂废水及其絮凝处理后废水进行分子量超滤分级试验。

本试验所用超滤器, 其主要技术参数为: 膜径 60mm, 操作压力 1~3kg/cm², 有效面积 21cm², 操作温度 20~40℃, 容积 150ml。

试验流程如图 1 所示。

试验用洗漂废水经定性滤纸抽滤, 主要目

的是去除 SS, 防止堵塞超滤膜。

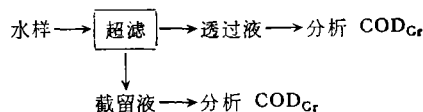


图 1 超滤试验示意图

超滤所需压力由外通 N₂ 满足。各废液体积及 COD_{Cr} 符号如图 2。

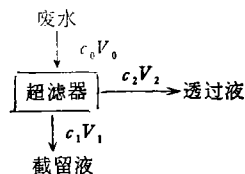


图 2 COD_{Cr} 数据的区别性划分

$V_0, c_0, V_1, c_1, V_2, c_2$ 分别代表废水、截留液、透过液的体积及测得的 COD_{Cr}。

假设废水、滤过液与截留液中小分子浓度(指小于截留分子量部分)分别为 $c'_{s0}, c'_{s2}, c'_{s1}$, 大分子浓度(指大于截留分子量部分)分别为 $c'_{b0}, c'_{b2}, c'_{b1}$ 。

对于 UF 膜来说, 有关系式:

$$c'_{s2} = c'_{s1} = c'_{s0}$$

$$\text{又: } c_0 = c'_{s0} + c'_{b0}$$

$$c_1 = c'_{s1} + c'_{b1}$$

$$c_2 = c'_{s2} + c'_{b2}$$

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透过液中: $c'_{b2} \doteq 0$

因而有 $c'_{s2} \doteq c_2$

所以 $c'_{s2} = c'_{s1} = c'_{s0} \doteq c_2$

因此, $c'_{b0} = c_0 - c'_{s0} \doteq c_0 - c_2$

从以上讨论可推知, 洗漂废水中小于截留分子量的 COD_{Cr} 值可由测定透过液的 COD_{Cr} 值得到. 洗漂废水中大于截留分子量的 COD_{Cr} 浓度可由原废水与透过液二者的 COD_{Cr} 之差得到.

二、试验结果与分析

洗漂废水 $\text{COD}_{\text{Cr}} = 1635.9\text{mg/L}$, 过滤后

(用 $\phi 15$ 定性滤纸)洗漂废水

$\text{COD}_{\text{Cr}} = 1517.7\text{mg/L}$,

絮凝处理后上清液 $\text{COD}_{\text{Cr}} = 604.7\text{mg/L}$, 洗漂废水超滤后透过液 $\text{COD}_{\text{Cr}} = 964.5\text{mg/L}$ (MW10000), 上清液超滤后透过液 $\text{COD}_{\text{Cr}} = 474.1\text{mg/L}$ (MW10000), 洗漂废水超滤后透过液 $\text{COD}_{\text{Cr}} = 600\text{mg/L}$ (MW3000), 上清液超滤后透过液 $\text{COD}_{\text{Cr}} = 469.8\text{mg/L}$ (MW3000). 数据整理如表 1. 从表 1 可以看出:

1. 洗漂废水中 $\text{MW} > 10000$ 与 $\text{MW} < 3000$ 是 COD_{Cr} 值的主要组成部分, 占 76%, 而二者的比例分别为 36.5%、39.5%, 相近.

表 1 不同截留分子量范围的 COD_{Cr} 值

分子量		MW	MW	MW
分类		>10000	3000~10000	<3000
COD_{Cr} 浓度 (mg/L)	洗漂废水 (1517.7)	553.2	364.5	600
	上清液 (604.7)	130.3	~0	469.8
	絮凝去除部分 (913.0)	422.9	364.5	130.2
COD_{Cr} 所占比(占洗漂废水总 COD_{Cr})(%)	洗漂废水 (100)	36.5	24.0	39.5
	上清液 (39.8)	8.6	~0	31.0
	絮凝去除部分 (60.2)	27.9	24.0	8.5

2. 絮凝处理去除的 COD_{Cr} 成分: MW 3000~10000 几乎全部被去除; $\text{MW} > 10000$ 的去除 76.4% (占该范围 COD_{Cr} 值), $\text{MW} < 3000$ 的去除 21.5% (占该分子量范围 COD_{Cr}). 未除去的主要是 $\text{MW} < 3000$ 的物质及部分 $\text{MW} > 10000$ 的物质, 分别占洗漂废水总 COD_{Cr} 的 31% 及 8.6%. 因此, 可根据废水中 $\text{MW} > 3000$ 物质的 COD_{Cr} 来近似推测通过絮凝可达到的 COD_{Cr} 去除率, 对絮凝方法处理废水有一定指导意义.

投加絮凝剂去除废水中的微小颗粒及胶体颗粒, 一般认为通过下列四种作用实现: ① 压缩双电层; ② 吸附中和; ③ 吸附架桥; ④ 絮体网捕. MW3000~MW10000 的物质全部被去除, 可认为此分子量间物质在颗粒大小、胶体性质方面, 均适于絮凝处理过程.

3. 比较絮凝后上清液经 MW10000 及 MW3000 超滤透过液的 COD_{Cr} 值, 分别为

474.4mg/L、469.8mg/L, 二者几乎相同, 可以认为 470mg/L 的 COD_{Cr} 值是絮凝处理后上清液的最低限值, 也就是假设 $\text{MW} < 3000$ 的 COD_{Cr} 去除量不变, 因此可以推得絮凝最大可能 COD_{Cr} 去除率为:

$$\begin{aligned} \text{COD}_{\text{Cr}} \text{ 可能去除率} &\leq \frac{\text{去除}(\text{COD})_{\text{max}}}{\text{洗漂废水 } \text{COD}_{\text{Cr}}} \\ &= \frac{1517.7 - 470}{1635.9} = 64.1\% \end{aligned}$$

再考虑到废水中:

$$\text{SS} = \frac{1635.9 - 1517.7}{1635.9} = 7.2\%$$

在 SS 可全被去除的情况下, 絮凝法处理试验用洗漂废水的最大 COD_{Cr} 去除率为:

$$(\text{COD}_{\text{Cr}}\%)_{\text{max}} \leq 64.1\% + 7.2\% = 71.3\%$$

此值比公认的絮凝物化法处理的实际效果 60—65% 高些.

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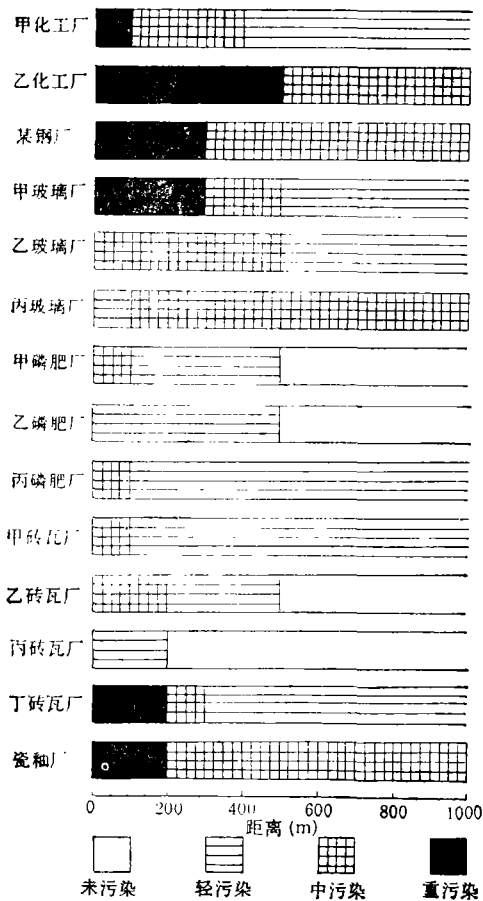


图5 环境要素的综合质量评价图

历史上的原因,上海各钢厂所用的生铁块大都需从外地运来,在两次化铁时消耗大量的萤石和能源,再加工工艺落后,设备陈旧(如土法烧结炉至今仍在沿用),造成有些钢厂附近的污染十分严重。国外一些先进的钢铁企业采用中性或酸性化铁炉化铁,已很少使用萤石作助熔剂。上海有的钢铁厂则改用中频电炉化铁,也不再使用萤石。新建的宝山钢铁厂把炼铁和炼钢实行连续作业,不用化铁炉,这样既节约能源,又避免了氟污染。这些都是减轻和控制氟污染的成功经验,值得推广。

(五) 改善作物配置,加强绿化工作。

如将开花期对氟敏感的水稻改种为其他抗氟性较强的经济作物(如棉、麻等),损失就可以大大减少。但

自从土地联产承包到户之后,每户的耕地面积有限,调节作物布局的机动余地很小,必须由主管农业的政府部门加以统一调配,才可使排氟工厂附近的作物得以合理的配置。

各种园林植物几乎都有不同程度的吸收和净化含氟废气的的能力。如甲玻璃厂的污染程度在综合质量评价(见图5)中并不算轻,但由于其厂外是一个树木众多的公园,其污染的影响就明显减小。而化工厂和瓷釉厂的污染之所以严重,在一定程度上是与这些厂附近几乎没有树木有关。因此大力加强绿化工作,扩大绿地面积,选种抗氟和吸氟力均较强的树种(如桑、杨、榆和悬铃木等),对改善各排氟工厂附近的环境和保护人体健康都有一定好处。

(六) 加强环境管理,定期监测各氟污染源对环境的影响。

氟化物是一种可以在环境中不断积累和转移的有毒污染物。有的排氟工厂在建厂初期未发现对人体有什么影响,但以后随着投产年限的延伸,逐渐发现氟斑牙发生率增加^[1],继而又发现氟骨症患者。这些都是难以康复的公害病,因此必须定期检查和监测各污染源对环境 and 人体健康的影响,及时消除各种隐患,力求做到防患于未然。

另外,我国现行的《工业“三废”排放试行标准(GB J4-73)》中规定,化工企业的烟囱高30m时,其氟化物的排放标准为1.8kg/h。据环保部门监测各排氟工厂的管道烟气排放量,绝大部分都没有超过这个标准,因此都不需缴纳含氟废气的排污费,同时也不需安装相应的治理设备。但据环境监测证明,各厂周围环境都已受到了不同程度的污染。说明上述标准中有关氟化物排放量的部分是订得过于宽松,应该予以修正,以发挥环境标准在管理工作中的应有作用。

参 考 文 献

- 1 吴方正等. 中国环境科学. 1984, 4(4): 19
- 2 城建部环保局. 环境监测分析方法. 北京: 中国环境科学出版社, 1983: 102-103
- 3 吴方正等. 蚕桑通报. 1982, (4): 16
- 4 舒金华. 环境科学. 1980, 1(4): 24
- 5 朱文江等. 中国环境科学. 1990, 10(5): 393
- 6 汪雅谷等. 中国环境科学. 1983, 3(3): 23
- 7 酆桂芬. 环境质量评价. 北京: 中国环境科学出版社, 1989: 40
- 8 朱文江等. 环境科学学报. 1989, 9(1): 105
- 9 朱文江等. 上海环境科学. 1989, 8(7): 38
- 10 朱文江等. 上海农学院学报. 1989, 7(4): 279

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4. 从以上分析可知,如进一步降低废水的 COD_{Cr} ,还须对 $\text{MW} < 3000$ 的小分子物质

考虑絮凝处理方法以外的方法。

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lake in summer was $1.02 \text{ mg/m}^2 \cdot \text{d}$. The total phosphorus release capacity from the sediments was estimated to be 1.346 t/y which is equivalent to 36.4% of the average annual external phosphorus loading. Sediment release of phosphorus is a major contributory factor for the eutrophication of the lake.

Key words: sediments, phosphorus, eutrophication.

Effect of Proper Ventilation on Improving Indoor Air Quality and Dweller's Health. Qiu Shicong, Chen Guifu (Wannan Medical College, Wuhu, Anhui): *Chin. J. Environ. Sci.*, **13**(3), 1992, pp. 29—32

An investigation on the natural ventilation in 417 rural dwellinghouses with children living in was carried out in south China from December 1988 to April 1989. Meanwhile, a follow-up observation of respiratory health conditions for the dwelling children was performed. An experimental model was also established to explore the possible improving measures. The results revealed that in 85% of the dwellinghouses, the times of air changes per hour (ACH) ranged from 0.5 to 1.0, and ACH was negatively correlated to the rate of respiratory symptoms (RRS) in the children ($P < 0.01$); when ACH was less than 0.5, the children's RRS was $3.52/100\text{pw}$, which is much higher than that of other groups with larger ACH; when room doors and windows were open, the ACH was 4 times as much as that when they were closed; moreover, closing doors and windows increased the indoor air concentrations of CO_2 , HCHO, and ^{222}Rn by 1—3 times; when the indoor air flow velocity was below 0.05 m/s the ventilation efficiency decreased to below 1.0, accordingly, the pollutants gradually accumulated and would finally impair the health of the residents. This study suggested that the proper arrangement of the ventilation in the light of the convection theory may effectively improve the air quality and thereby the health conditions of the residents.

Key words: ventilation in dwelling-house, indoor air quality, health efficiency.

Evaluation of the Pollution in Lake Dianchi with Zooplankton as Indicator. Huang haikui, Zhao Jia-chong (Kunming Municipal Institute of Environment Science): *Chin. J. Environ. Sci.*, **13**(3), 1992, pp. 33—36

Analysis of the species and mass population of zooplankton was carried out by means of Sander's sparse curve and Shannon-Wiener's diversity index on different regions of lake Dianchi. Integrated with the output of the analysis of zooplankton indicator distribution, the following results were obtained: (1) the extent of pollution is obviously different in the inflake from the outlake i. e. the inflake is in α stage of pollution and the outlake is in β stage. (2) the gravity of pollution in different regions of lake Dianchi are: the exit of river Xinhe > the exit of river Daguang > the center of inflake > Huiwan > Darhewei > the middle of Guanyinshan. (3) the inflake is in the process of swamping.

Key words: lake Dianchi, zooplankton, pollution indicator, Sander's Sparse curve, Shannon-Wiener's diversity index.

Catalyst for Removing Carbon Monoxide at Room Temperature. Li Chunhua, Xu Hongbing and An Lidun (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou): *Chin. J. Environ. Sci.*, **13**(3), 1992, PP. 37—39

Activated carbon compound carrier supported noble metal catalysts for the catalytical oxidation of CO were investigated in the following aspects: selection and preparation of supports and precursors of active components as well as preparation conditions of the catalysts. Results show that CO-20-2 catalyst made in this work can remove CO completely at room temperature. Both of its activity and stability are better than the catalysts available now.

Key words: palladium and platinum catalysts, carbon monoxide oxidation, activated carbon complex support.

Study on Pollution Contributions from Traffic in Beijing City. Han Zhixiong, Xing Yulan, Quan Baoling (Beijing Municipal Research Institute of Environmental Protection): *Chin. J. Environ. Sci.*, **13**(3), 1992, pp. 40—42

This paper clearly defines the conceptions for both road and regional pollution contributions and gives a set of methods for the calculation of regional pollution contribution. As an example, the pollution contributions of CO, NO_x , and THC, which are major pollutants from vehicles, were studied for a central area of 158 km^2 of Beijing city. The study shows that the regional pollution contributions for CO, NO_x and THC reached 14.3%, 32.2% and 86.6% in winter and 58.4%, 68.7%, and 86.6% in fall, respectively. While, the road pollution contributions for CO, NO_x and THC reached 65.7%, 71.6%, and 37.6% in winter and 58.8%, 75.5% and 67.5% in fall, respectively.

Key words: air pollution, traffic pollution.

Assessment of the Maximum Removal Rate of Pulp-making Waste Water with Flocculation Treatment by UF Technology. Cheng Yanjun (Environmental Protection Institute, Ministry of Light Industry): *Chin. J. Environ. Sci.*, **13**(3), 1992, pp. 43—44

Relative molecular weight fractions of COD in the waste water were determined by UF technology, so as to estimate the maximum removal rate of COD with flocculation-treatment. It has been found that most of the COD in the water is associated with the fractions having molecular weight greater than 10000 or smaller than 3000; the maximum removal rate of COD is 71.3%.

Key words: UF, Flocculation, Pulp-making waste water, COD.

A Study on Denitrification of Coke-plant Wastewater through a Biological Process Wen Yibo