超滤及其组合工艺对污水的深度处理试验

王　锦[1]，　曹　宇[2]，　王晓昌[1]，　李志华[1]

(1. 西安建筑科技大学环境与市政工程学院，西安　710055；　2. 西安市北石桥污水净化中心，西安　710086)

摘　要：超滤及其组合工艺，混凝-UF 和粉末活性炭(PAC)-UF 对污水深度处理的试验结果表明，超滤对水中浊度几乎可以完全去除，对细菌和大肠杆菌的去除效率大于 99 %，对水中有机物、氨氮、总铁和总锰也均有一定的去除。超滤前加混凝预处理或粉末活性炭吸附后，提高了水中有机物的去除率，同时减轻了膜污染，提高了膜通量和产水量。此外，三种工艺在等量冲洗用水的条件下，适当缩短过滤周期，增加反冲洗频率均提高了单位能耗产水量。

关键词：混凝；　超滤；　粉末活性炭；　膜污染；　产水量

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在水资源日益匮乏的今天，污水回用已是大家的共识。国外对低压膜过滤技术的应用已不局限于饮用水，正逐步扩展到污水处理领域[1~2]。我国目前对超滤在水处理方面的应用多集中于给水的深度处理，而直接超滤或以超滤为核心的组合工艺对污水深度处理回用的研究和应用较少。为了考察超滤对污水处理回用的适用性，我们以西安北石桥污水净化中心二级处理水为原水进行了现场处理实验，着重研究了直接超滤和混凝-超滤，粉末活性炭-超滤组合工艺的处理效果和膜污染情况。

1　试验方法

1.1　试验装置

采用的工艺流程如图 1 所示。超滤组件采用截留分子量为 10 万的国产中空纤维膜，材质为聚丙烯腈(PAN)，加压方式为内压式。只有在混凝-超滤工艺中才增加管式混合器，其它两种工艺中相应位置为管道。

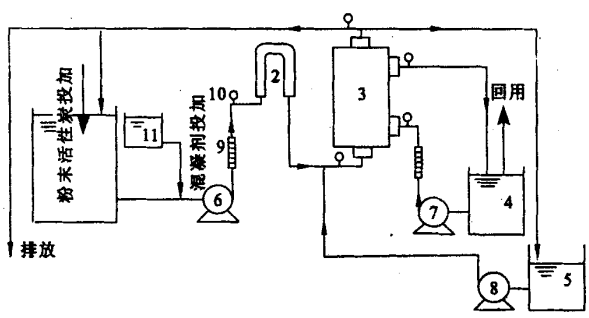

图 1　试验装置简图

1. 原水箱　2. 管式混合器　3. 超滤组件　4. 渗透液水箱　5. 化学清洗水箱　6. 原水泵　7. 水力反洗泵　8. 化学清洗泵　9. 流量计　10. 压力表　11. 混凝剂药箱

作者简介：王锦(1973 -)，女，博士研究生，目前主要从事水处理膜技术的应用研究。

1.2　试验方法

试验原水为西安北石桥污水处理厂二沉池出水。试验分为三种工艺：一是原水直接超滤；二是混凝-超滤组合，混凝剂为精制硫酸铝($Al_2(SO_4)_3 \cdot 18H_2O$)，投药量以铝离子浓度计为 7mg/L，采用泵前投药，水泵混合和管式混合器混凝，停留时间为 1min 左右，G 值为 $10s^{-1}$，属于微絮凝条件，混凝后颗粒的 ζ 电位保持在 0mV 左右，加药后水的 pH 在 7 左右。三是粉末活性炭(PAC)-超滤，所用粉末活性炭为 150～160 筛目，相应粒径为 100μm，低于膜孔内径(0.85mm)的五分之一，不会堵塞膜孔道，粉末活性炭投量为 25mg/L，在原水中的水力停留时间约为 1h。

每种工艺的试验分为两种操作参数，长周期过滤和反冲(过滤 30min，反冲 4min)及短周期过滤和反冲(过滤 15min，反冲 2min)。反冲用水为滤后水。每组实验后将膜用碱液(NaOH 配制到 pH≈11)循环清洗 1h，然后水力清洗干净，使膜通量恢复到初值。试验采用交叉流式(cross-flow)，每组试验回收率保持在 80 %，过滤压力 0.1MPa，反洗压力 0.12MPa。

1.3　试验数据处理方法

超滤膜的平均半透膜压通过 Tutujian 公式计算：

$$P_{tm} = [(P_i + P_o)/2] - P_p$$

式中，P_{tm}为半透膜压；P_i 为膜组件进口处的压力；P_o 为膜组件出口处的压力；P_p 为渗透液压力。

整个试验过程中温度为 21 ±2 ℃。在压力保持恒定的情况下，通量表示膜的产水量，从其变化可了解膜的污染状况，而比渗透通量 K_W，即通量与半透膜压的比值，可在无需保持压力恒定的情况下用以监测膜污染的状况。

为了比较三种工艺及不同操作参数对膜污染的影响，计算出单位能耗的净产水量作为评价指标。计算方法如下：

净产水量等于总生产水量减去反冲洗用水量,即 $V_{net} = V - V_{bf}$

总耗能包括进水泵和反洗泵在整个试验周期内的耗能量。浓缩液循环的耗能量部分,实际上是间接利用原水泵作为循环泵的,故该项耗能不再单独计算。

进料泵耗能为操作压力,进料流量和过滤时间间隔的乘积总和,即 $E_f = \sum(P_f Q_f D_f)$

反洗泵耗能为反冲洗压力,反洗流量和反洗时间间隔的乘积总和,即 $E_{bf} = \sum(P_{bf} Q_{bf} D_{bf})$

总耗能为进料泵耗能和反洗泵耗能之和,即 $E_{tot} = E_f + E_{bf}$

单位耗能的净产水量 $R = V_{net} / E_{tot}$

2　试验结果

2.1　超滤的消毒作用

超滤的消毒作用如表 1 所示。

表 1　超滤的消毒作用

项目	测试方法	原水	渗透液	去除率
细菌总数	平板计数	1700～5100 个/ mL	< 50 个/ mL	> 99 %
大肠杆菌	最可能数	1200～3000 个/ 100mL	< 3 个/ 100mL	> 99 %

从表 1 可以看出,污水中的细菌总数和大肠杆菌含量均较高,但超滤对其去除率均大于 99 %。这是因为超滤膜的孔径一般小于细菌的尺寸,因此细菌或大肠菌均可通过超滤得以去除。

2.2　超滤及其组合工艺的处理水质

直接超滤及其组合工艺的处理水质如表 2 所示。

表 2　超滤及其组合工艺处理水质

项目	原水	直接超滤	处理水 混凝-超滤	粉末活性炭-超滤
浊度(NTU)	4～20	< 0.1	< 0.1	< 0.1
色度(铂-钴比色法)	25～35	20～30	15～25	15～20
UV_{254} (cm^{-1})	0.106～0.163	0.101～0.137	0.028～0.07	0.044～0.081
DOC(mg/ L)	4.25～9.43	3.27～6.68	2.85～5.93	3.05～6.12
COD_{cr} (mg/ L)	10.8～41.2	7.3～16.1	5.5～10.3	6.5～12.2
BOD_5 (mg/ L)	6～12	2～4	2～3	2～3
氨氮(mg/ L)	0.70～2.04	0.63～1.63	0.66～1.68	0.70～1.34
总铁(mg/ L)	0.43～0.83	0.21～0.33	0.10～0.24	0.20～0.33
总锰(mg/ L)	0.25～0.41	0.14～0.2	0.08～0.16	0.17～0.24
总硬度(mg/ L)	101.0	100.0	99.0	99.0

注:除 BOD_5 采用美国 HACH 的 BOD 仪(Model-2173B)测定外,其余指标均按照标准方法[3]测定。

从表 2 中可看出,超滤工艺对原水中的浊度物质几乎能够百分之百地去除。对色度物质的去除以粉末活性炭-超滤组合工艺为最优。与直接超滤相比,超滤组合工艺提高了对有机物的去除率。BOD_5 反映了水中可生化降解有机物的总量,这部分有机物以饱和构造为主,分子量相对较高,因此超滤出水的 BOD_5 含量较低。三种工艺对于氨氮都有一定的去除,但去除率差别不大。与其它两种工艺相比,混凝-超滤工艺对总铁和总锰的去除较高,这可能是因为高价铁、锰与混凝剂作用,生成氢氧化铁等沉淀从而被膜截留。但三种工艺对水中硬度几乎都没有去除作用。

2.3　超滤及其组合工艺膜渗透通量的变化

超滤及其组合工艺在长周期和短周期过滤和反冲条件下的比渗透通量变化如图 2 所示。

从图 2 中看出对于直接超滤,长周期过滤和反冲洗并未使通量得到有效恢复,尤其是过滤初期 2h 内通量下降尤为显著,过滤 10h 后,通量降低到初始值的 35 %。与此相比,短周期过滤和反冲洗使通量有很明显的恢复,过滤 10h 后,通量降低到初始值的 70 %。整体来看在不增加反冲洗总水量的情况下,反洗频率增加一倍,通量下降也减少了一倍。对于混凝-超滤,长周期条件下过滤 10h 后,通量稍有下降,为初始值的 85 %,而短周期条件下在整个过滤周期内通量没有下降。对于粉末活性炭-超滤,长周期条件下过滤 10h 后,通量有一定的下降,为初始值的 78 %,而短周期条件下,通量稍有下降,为初始值的 91 %。因此三种工艺均在短周期条件下连续运行时通量下降缓慢,这说明短过滤时间,高频率反冲有利于缓解膜的污染,而长时间过滤及长时间连续横向流剪切作用使膜表面的滤饼层变得厚实而且密实,阻力增大,降低了水力反冲洗的效果。

对于三种工艺的比较,以直接超滤对膜污染的程度最为严重,混凝 - 超滤膜污染的程度最轻,粉末活性炭 - 超滤居中。这说明组合工艺一定程度上缓解了膜污染。投加混凝剂的主要目的是将小分子有机物或胶体形成较大的絮凝体,从而被膜表面截留,形成疏松滤饼层,并有效防止膜孔内污染。投加粉末活性炭可有效吸附水中低分子量有机物,使溶解性小分子有机物转移至固相,从而被超滤膜截留,降低膜孔内污染,从而使超滤保持较高渗透通量。

2.4　超滤及其组合工艺的单位能耗产水量比较

以超滤为核心的三种工艺在长周期和短周期操作条件下的单位能耗净产水量如表 3 所示。

表 3　超滤及其组合工艺两种操作参数下单位能量的净产水量比较　(m^3/ kW·h)

操作参数	直接超滤	混凝-超滤	PAC-超滤
过滤 30min,反冲 4min	20.3	21.7	19.3
过滤 15min,反冲 2min	22.6	25.6	23.8

单位能耗净产水量作为评价指标可较为全面地分析工艺和操作参数的性能。从表 3 可知对于三种工艺,过滤 15min,反冲 2min 的操作条件下单位能耗产水量都比过滤 30min,反冲 4min 的操作条件下有所提高。另外,三种工艺在两种操作条件下,以混凝-超滤

工艺的单位能耗产水量最高,而直接超滤和粉末活性炭-超滤两种工艺较为接近。

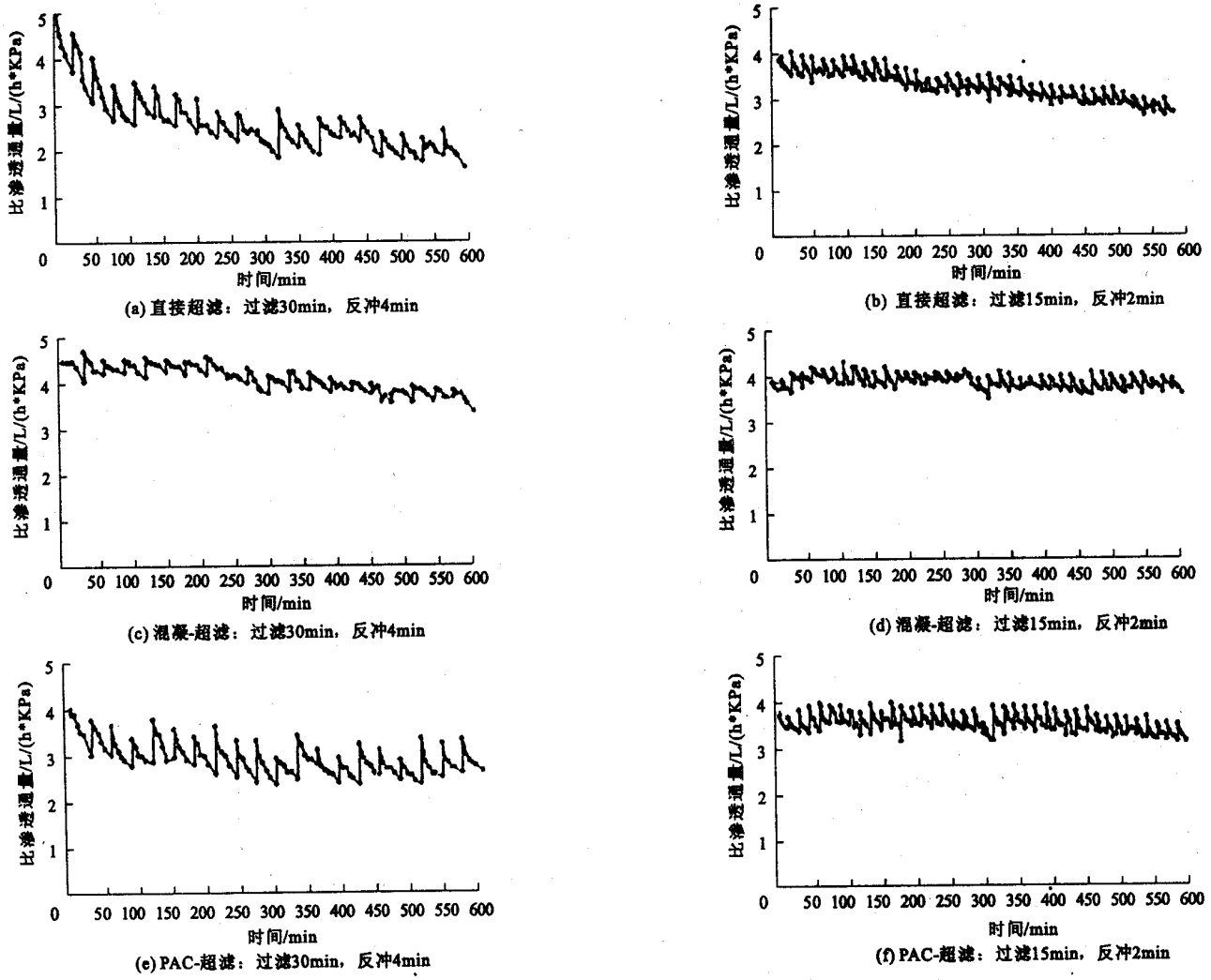

图 2 超滤及其组合工艺两种操作参数下的比渗透通量变化

3 结论

(1)超滤对细菌总数和大肠杆菌有很好的去除效果,去除率均大于 99 %。

(2)超滤及其组合工艺对浊度几乎能完全去除。与直接超滤相比,混凝-超滤和粉末活性炭-超滤组合工艺提高了对有机物的去除率。另外,超滤对总铁、总锰也有一定的去除效果,尤其是混凝-超滤的效果最为显著。

(3)三种工艺中以混凝-超滤对膜的污染最轻,通量下降最慢,单位能耗产水量最高。

(4)在反冲洗水量相同的条件下,较短的过滤周期和较频繁的水力反冲洗能使膜渗透通量维持在较高的水平,从而增大单位能耗产水量。

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Experiment Studies of Effect of CO_2 on NO Reduction in CH_4 Flame

XU Min, QIU Jian-rong, LI Jun
(State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430072)

Abstract: Systematic experiments on the effect of CO_2 on NO reduction in CH_4 flame were carried out. It was found that various stoichiometric ratios had a pronounced influence on reduction of CO. Compared to the condition of lean fuel, NO reduction ratio is higher under the condition of rich fuel. Existence of CO2 has a positive effect on NO destruction, but on the contrary, CO_2 gives a negative effect evidently on NO destruction under rich fuel condition. It was also noticed that the negative effect of CO_2 on NO destruction under rich fuel condition faded out with the continuous increase of CO_2 concentration.
Keywords: O_2/ CO_2; NO; reduction

Studies on Photo-catalytic Degradation of Perovskite-type Oxides: $LaFeO_3$ and $SrFeO_{3-\lambda}$

SONG Li-xia, FU Xi-xian, YANG Qiu-hua, SUN Yi-huan, WANG Jun-zhen
(Department of Chemistry, Tianjin University, Tianjin 300072)

Abstract: Degradation experiments of various water-soluble dyes were performed in a suspension system of $LaFeO_3$ and $SrFeO_{3-\lambda}$ prepared by citrate method. A fluorescent Hg lamp was used as irradiation source. The experimental results presented evident photo-catalytic activities of perovskite-type oxides, of which $SrFeO_{3-\lambda}$ showed stronger activities than $LaFeO_3$. This is attributed to the unique electronic structure of the ion A(La^{3+}, Sr^{2+}).
Keywords: $LaFeO_3$; $SrFeO_{3-\lambda}$; photo-catalytic activity; water-soluble dye

Applying Geo-accumulation Index to Assess Heavy Metal Pollution in Sediment: Influence of Different Geochemical Background

TENG Yan-guo[1], TUO Xian-guo[2], NI Shi-jun[2], ZHANG Cheng-jiang[2]
(1. Institute of Environmental Science, Beijing Normal University, Beijing 100875; 2. Chengdu University of Technology, Chengdu 610059)

Abstract: Müller index of geo-accumulation or Igeo is a widely recognized index for metal pollution that indicates the level of contamination found in sediments. In this paper, influence of different geochemical background selected was discussed when the assessment was made using Igeo. To reduce the influence, it is suggested that the geochemical background selected be in close relation to the sediment.
Keywords: geo-accumulation index; sediments; heavy metal pollution; geochemical background

Studies on Degradation of Dimethyl Phthalate Using Micellar Electrokinetic Capillary Chromatography

LI Hai-yan, SHI Yin-tao, ZENG Qing-fu
(The Research Center of Environmental Science, Wuhan Institute of Science and Technology, Wuhan 430073)

Abstract: Processes of dimethyl phthalate degradation in aqueous solution by ozonation and TiO_2- photo-catalytic oxidation respectively were investigated. Characterization of the intermediates and the end products were determined by means of micellar electrokinatic capilliary chromatography. The preliminary results showed main intermediate product by ozonation was phthalate acid that went through oxidation further. However, TiO_2- photo-catalytic oxidation of dimethyl phthalate follows a free radical-free mechanism, directly breaking benzene rings with the end products: CO_2 and H_2O.
Keywords: dimethyl phthalate; oxidation degradation; micellar electokinatic capillary chromatography

Preliminary Studies of Chitin as Immobilized Micro-organism Media for Treating Wastewater

LI Fei-li, XU Lu-sheng, PAN Li-li
(School of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310014)

Abstract: This paper describes a series of processes of bio-chemical wastewater treatment using chitin as immobilized micro-organism media. Factors that influence the efficiency of an activated sludge system were investigated and optimum dosage of chitin was determined by trade-off studies. The preliminary studies with pharmaceutical wastewater, dyeing wastewater and domestic sewage respectively have showed that treatment with chitin addition is better in terms of COD removal and shock loading buffering in comparison with conventional activated sludge as well as powdered activated carbon addition methods.
Keywords: chitin; immobilized micro-organism; biochemical treatment

Ultra-filtration and Its Hybrid Processes for Tertiary Treatment of Sewage

WANG Jin[1], CAO Yu[2], WANG Xiao-chang[1], LI Zhi-hua[1]
(1. School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055; 2. Xi'an Bei Shi Qiao Sewage Purification Center, Xi'an 710086)

Abstract: Experiments of treating the effluent from a sewage secondary treatment plant by UF and UF plus coagulation or powdered activated carbon (PAC) were carried out. The results show UF removes turbidity completely, more than 99 % bacteria and E-coli and a certain amount of organic matters, ammonia nitrogen and manganese. Hybrid processes featuring UF preceded by coagulation or PAC enhance the removal of organics, and moreover, reduce UF membrane fouling, improving flux of membrane. According to the experimental study, it is concluded that a shortened filtration period and increased backwash frequency result in higher water yield per unit energy consumption with same amount of backwash water.
Keywords: UF; coagulation; powdered activated carbon; membrane fouling; water yield

Application of Electro-catalysis Technology for Treatment of Landfill Leachate