研究报告

超滤法处理回用印钞厂擦版液的研究

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摘要 根据擦版液的特性,选择了适合处理擦版液的单皮层内压式中空纤维超滤膜,对超滤过程中的操作压力、料液温度、料液流速和固含量等工艺参数以及清洗药品和方法进行了研究。结果表明,当进口压力为0.17MPa,膜面流速在2.7m/s左右,循环液温度在40℃左右时,透水速度可达到50—60L(m.h)。操作过程中,只用透过液作简单清洗即可使透水速度得到较好的恢复。只有当透水速度衰减严重时,才在70℃条件下进行化学清洗,而且可以使透水速度得到较为彻底的恢复。化学清洗周期至少在1星期以上。

关键词 中空纤维超滤膜,印钞废水,超滤法,废水回用。

目前国内印钞业对擦版液的处理多采用絮凝-抽滤法,滤出液仍须进一步处理,有的甚至直接排放,对环境造成严重污染。近年来随着膜科学技术的发展,国处已有厂家采用超滤技术处理印钞厂的擦版液。由于超过滤是一个纯粹的物理过程,擦版液经过膜超滤,透过液中保留了原液中的NaOH和表面活性剂等有用成分,稍作调整即可回用。国内尚未发现超滤法处理印钞厂擦版液的报道。中国科学院生态环境研究中心采用近年来的科研成果,和北京印钞厂合作,进行了用膜技术处理擦板液的应用研究,取得了较好的效果。

1 实验

1.1 超滤膜及装置

(1)根据擦版液的物化特性以及清洗工艺的特殊要求,在对不同材质膜的实验比较基础上,选择了耐油墨污染,耐高温清洗和耐高pH值腐蚀的聚砜共混中空纤维超滤膜,如图1所示。该膜系内压式单皮层中空纤维膜,其内壁为分离层,外壁为开孔结构。透过内皮层的小分子溶质不会被外壁所堵塞,而且反清洗效果较好。纤维内径为1.0mm,壁厚为0.3mm,截留分子量为20000道尔顿,中国科学院生态环境研究中心研制。

(2)中空纤维膜组件,Φ25×1090mm有效膜面积约0.4m,中国科学院生态环境研究中心生产。

(3)中空纤维超滤器,型号:DC10LA,美国Amican公司生产。

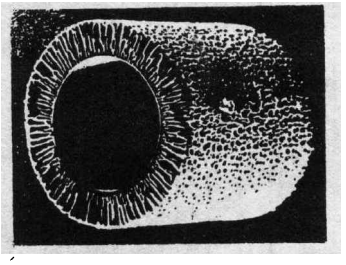

图1 中空纤维超滤膜断面图

1.2 分析方法

擦版液中主要成分为去离子水、油墨、表面活性剂、碱和石蜡等,本工作的主要目的是去除擦版液中的油墨,对水和其他有用成分进行回用。透过液中的油墨用比色法进行分析,膜对油墨的截留率接近100%,故在结果和讨论中不作

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叙述。

1.3 工艺流程

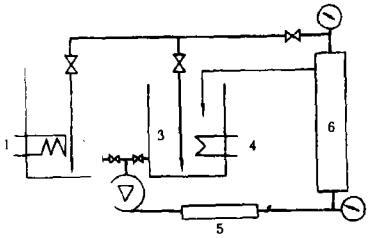

图2 超滤工艺流程

1、热交换器 2、循环槽 3、清洗槽

4、电加热器 5、预过滤器 6、超滤器

本工作采用间歇式操作，考虑到生产工艺和清洗的要求，在循环槽和清洗槽中分别安装了换热器。图2为本工作的工艺流程示意图。

2 结果和讨论

2.1 操作压力对膜透过液速度的影响

超滤过程是以压力为驱动力的分离过程，所以操作压力是影响膜过程的主要因素之一。如图3所示，在膜面料液流速为0.27m/s，温度为30℃，料液含固量为12%的条件下，每提高平均压力0.01MPa，可增加透水速度4.5%。考虑到中空纤维的强度因素，建议在平均压力为0.1—0.12MPa条件下操作，进口压力最好保持在0.15—0.2MPa之间。

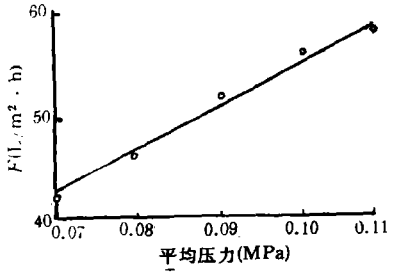

图3 超作压力对膜性能的影响

料液温度：30℃，含固量：—11%，料液流速：2.8m/s

2.2 膜面流速对膜性能的影响

膜面流速是按膜内孔截面积计算的原液流速。膜面流速的大小，表示膜压力侧循环液流动的流体力学状况。实验表明，随着膜面流速的增加，循环液湍程度增加，膜浓差极化和污染减小，因而膜的透液速度也随之增加。结果如图4。可见在固定操作压力，料液温度和固含量的条件下，膜面流速每提高0.1m/s，透水速度可增加5%，而且衰减速度显著降低。对于擦版液这样的高浓度料液，膜面流速最好保持在2.8—3.0m/s之间。

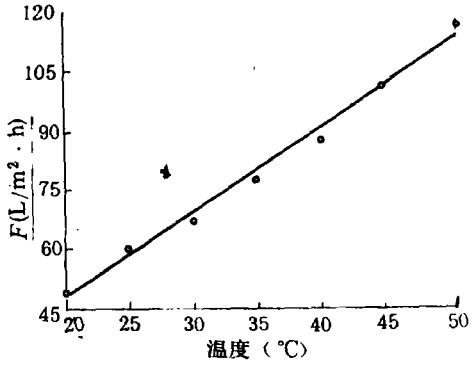

图4 料液流速对透水速度的影响

平均压力：0.1MPa，料液流速：2.7m/s，含固量：—11%

2.3 进料液浓度对膜性能的影响

在间歇式超滤过程中，随着透过液不断流出，循环料液体积逐渐减少，使得料液中固体浓度不断增加，这直接影响膜的透液速度。图5说明了在膜面流速固定的前提下，透液速度随着固体含量的增加有下降趋势。一般来说，随着液体浓度增加，溶液粘度增大，膜面上浓度极化和污染愈加严重。但由于该体系中含有表面活性剂，在固含量小于10%时，曲线下降斜率并不大；在固含量大于10%时，曲线下降斜率突然变大，说明浓度在这个范围内有固体物在膜面上迅速聚集，导致透液速度迅速下降。

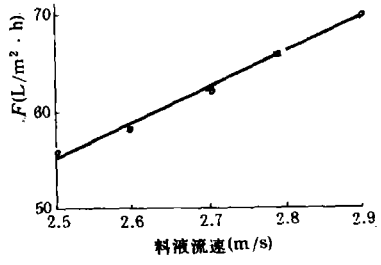

图5 料液浓度对膜性能的影响

力：0.1MPa，料液流速：2.7m/s，料液温度：30℃

2.4 循环液温度对透液速度的影响

本工作中温度是影响膜性能最重要的因素之一，图6显示了透水速度随温度变化而变化的趋势，可以看出，透液速度随温度的升高而明显

上升，温度平均每升高1℃，透液速度可增加2%—2.5%左右，这是因为料液随温度升高其粘度降低造成的结果。可见在生产工艺许可的条件下，提高料液的操作温度，是提高超滤效率，降低投资强度的行之有效的措施之一。

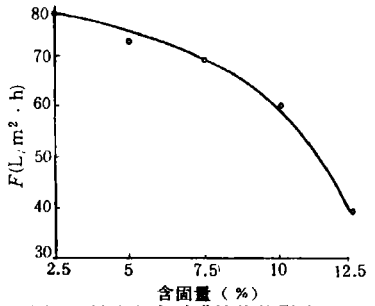

图6 料液温度对膜性能的影响

力：0.1MPa，料液流速：2.7m/s，固含量：－11%

2.5 运行时间对超滤速度的影响

从图7中可以看出，透液速度随运行时间的增加，没有降低趋势。这可能是此液体中含有表面活性剂，对膜面的污染不严重，渗透液粘度也比较低，膜面的流速较快，并采取了有效的清洗方法，所以得到比较理想的结果。另外从膜断面的着色程度看，在设备运行200多h后，膜对油墨并无吸附污染的迹象，说明聚砜共混超滤膜是适合处理擦版液的较好膜品种之一。

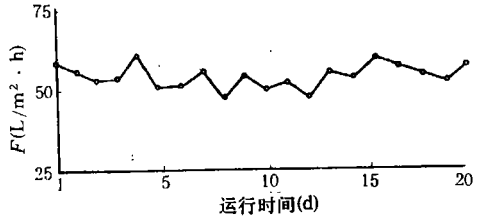

图7 运行时间对膜性能的影响

平均压力：0.1MPa，料液流速：2.7—2.9m/s，

料液温度：30℃

2.6 超滤膜的清洗

在超滤运行的过程中，膜面上的积存物一般随运行时间的增加而增加，因而导致透液速度下降。若不及时清洗膜，则会影响超滤效果。此实验采用间歇式运行，在每次停机之前，用清洗溶液只需运行3—5min。在下次运行之前把清洗液排出，然后加擦版液继续运行。只是在透水速度下降严重时，才进行化学清洗。可以看出，在设备运行16d后，通过化学清洗，透水速度基本恢复到了初始的水平。

表1 超滤膜的清洗效果[1)]

序号	清洗方式	清洗温度（℃）	清洗压力（MPa）	透水速度（ml/min）
1	正常清洗[2)]	28	0.09	550
2	正常清洗	23	0.1	565
3	正常清洗	29	0.1	400
4	化学清洗[3)] 20min后	26	0.1	480
5	正常清洗	26	0.1	405
6	正常清洗	30	0.1	440
7	正常清洗	24	0.1	370
8	正常清洗	14	0.1	460
9	正常清洗[4)]	27	0.1	520
10	正常清洗	20	0.1	455
11	化学清洗后[5)]	14	0.1	510
12	正常清洗	16	0.1	520

1)正常清洗在室温下进行，化学清洗在70℃情况下进行；2)起始；3)第6d清洗，运行1d后正常清洗时测；4)第12d50℃清洗；5)第16d清洗30min。

2.7 超滤后浓溶液的处理

擦版液经过超滤处理，80%液体可透过膜，再经过浓度调整，可重新作为擦版清洗液继续使用，剩下20%的循环液可经过短时间沉淀，上清液可进入超滤循环槽，下层浓液可经过絮凝-抽滤处理，最后成为固体废碴，统一进行处理。

3 结论

结果表明，单皮层聚砜共混中空纤维超滤膜是处理擦版液的较好膜品种，透明浅黄色滤液中基本没有油墨颜料。当进口压力为0.17MPa，膜面流速在2.7m/s左右，循环液温度在40℃左右时，透液速度可达50—60L/(m.h)。本工作清洗方法简单，有效，对膜具有较高的恢复率。在长期操作过程中性能稳定，清洗周期长。

致谢 本工作得到刘福谅、韩式荆、刘忠洲研究员和北京印钞厂领导的热情帮助和指导，在此仅表谢意。

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Based on the property of the banknote printing effluent studied, the polysulfone blend hollow fiber menbrane with single skin was choosen. The technical parameters of ultrafiltration, such as operating pressure, curent velocity, temperature and cleaning reagent, procedure were determined. The results show that when the process operated at an enter pressure of 0.17MPa, recycle feed temperature of about40℃ and a curent velocity of about 2.7m/s, the flux could be 50-60L/m·h. Normally the permeate rate can be restored better only through a simple cleaning with the permeate. When the permeate rate ca was declined sianificantly, a chemical cleaning would be necessary to be taken at a temperature below 70℃. The cleaning period was at least 7 days.

Key words: hollow fiber menbrane, printing banknote effluent, ultrafiltration, wastewater recycle.

Treatment of High Concentration Copper-COD Wastewater. Zhang Zhongyan et al. (Shanghai University of Technology): *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 37—41

A combined chemical coagulation-biological fluidized bed process has been used to investigate the treatment of wastewater in whieh the concentrations of copper and COD are 1700—3800mg/L and 3900—5400 mg/L, respectively. The relations between the copper and COD removal rates and the technical conditions of the process, such as retention time, load in influent water, the ratio of gas to water etc. for the fluidized bed; pH and coagulant dosages etc. for coagulation process, have been determined. The results show that the above conbined process is the effective one for high concentration copper-COD wastewater. Under the optimum conditions, the copper and COD concentrations in the effluent can be less than 0.82 mg/L and 180 mg/L respectively, and the total removal rates can be obtained of up to 99.97% for copper and 95% for COD.

Key words: chemical coagulation, fluidized bed, copper, organic wastewater, wastewater treatment.

Observation and Analysis on the Radiative Effects of the Lanzhou *Winter Urban Smog Layer*. Su Wenying et al. (Department of Atmospheric Science, Lanzhou University, Lanzhou 730001): *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 42—47

In winter, there is a dense smog layer over Lanzhou city. In this paper, use the radiative and sonde data obtained in December 1990 at Lanzhou University and at the top of the South-mountain which is 625 m high to analyse and calculate the radiative effects of the smog layer. The Lanzhou urban smog layer is characterized by a high turbidity coefficient and a low wave length exponent, and decreases the solar radiation significantly. The average heating rate of the smog layer is 6.16 ℃/dvwith maximum turbidity coefficient. The smog layer has different extinctionsto different wave intervals and has a strongest extinction to the visible part. The smog layer causes the counter radiation reaching Lanzhou surface 5.2% more than that of the South-mountain, total incoming radiation is 5.6% less than that of the South-mountain, and surface radiation balance is 67.8% less than that of the South-mountain. The existence of the smog layer increases the stability of the urban boundary layer.

Key words: urban smog layer, short-wave heating, long-wave cooling rate, extinction coefficient, surface radiation balance.

Application of the Face Graph and Geo-accumulation Index Method to the Comprehensive Assessment of Pollution by Heavy Metals in Sedimdent. Zhao Zhijié wt al. (Departmennt of City and Environmental Science, Peking University, B eijing 1000871): *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 48—52

Based on the sedimentation principles and environmentally chemical characteristics of heavy metal, and using internationally new methods on heavy metal pollution assessment with multi-variable graph expression—face graph, a synthtical assessment study has been made on the state of heavy metal pollution and geo-accumulation of heavy metals in Taizi river sediment in Benxi reach. The results indicated that the state of heavy metal pollution of Taizi river in Benxi reach is very serious, and appropriate counter measures should be taken.

Key words: multi-variable graph—face graph, heavy metal pollution, geo-accumulation index.

Study on Arsenic Speciation in the environment. Wang Chunxu, Li Shengzhi et al. (Hebei Normal University, Shijiazhuang 050016): *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 53—57

Different arsenic species in soils, sea waters, marine organisms and urine are determined by using the hydride generation-electrothermal quartz furnace-atomic absorption spectrometry. The results indicates that the inorganic arsenic is a major part of arsenic in soils and As (V) is major part of inorganic arsenic. Methylated arsenic species is important in sea waters and urine. Moreover MMAA and DMAA are significant fractions in marine organisms.

Key Words: electrothermal quartz furnace; Atomic absorption spectrometry; arsenic species.

A Study on the Natural Mineral Manganese Catalytic Oxidation Process for the Treatment of Sulfur-bearing Wastewater. Chen Tianhu, Wang Jiaquan. (Hefei University of Technology, Hefei 230009): *Chin. J. Environ. Sci.* **14**(4), 1993, pp. 58—61

A cheep natural mineral manganese was used as a catalyst to catalytically oxidate sulfur-bearing wastewater at the ambient temperature and pressure. When the wastewater has a sulfur concetration of 100—400mg/L, and is treated in a 10L reactor at pH 9-10, with an air flow of 0.1m³/h and a catalyst dose of 100—150mg/L for 4 hours, the removal of sulfur from wastewaster reaches 94%—98%. As compared with the similar process without catalyst, the present process has a reduced air volume and time for aeration, about 30% reduction in energy consumption, and about 20% reduction in treatment cost. The results show that Using this King of cheep natural mineral manganese as a catalyst to catalytically oxidate sulfur-bearing wastewater is an effective method.

Key words: natural mineral manganese, catalytic oxidation, sulfur-bearing wastewater.

An Anaerobic Reactor for the treatment of Organic Wastewater Containing High Suspended solids. Shen Lixian et al. (Beijing Municipal Research Institute of Environmental Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **14**(4), 1993, pp. 62—65

The reactor used in this study combined the features of UASB and two-phase digestion reactors. Acidification, methanogenesis digestion and settling clarification are effectively integrated in one reactor. The return mixing by produced biogas and the liquid is achieved and no energy and equipment are needed. The problems