Transactions of Tianjin University
Vol. 8 No. 3 Sep. 2002

Micro-Polluted Surface Water Treatment by PAC-MBR Process *

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Abstract: A kind of hybrid membrane process, which integrated powdered activated carbon (PAC) with membrane bioreactor (MBR), was designed for bench scale experiment for micro-polluted surface water treatment. Molecular weight analysis was used to evaluate the efficiency of each unit process and the integration of them. The result of analysis indicated that organic molecules in the treated water from PAC-MBR process were concentrated on the section of below 1000, while PAC adsorption could enhance the removal efficiency of this section due to the high percent of biodegradation recalcitrant organic matter with low molecular weight. It was demonstrated that PAC adsorption and biological treatment promoted each other in PAC-MBR process, with a removal efficiency of 70 % for COD_{Mn} and UV_{254}, 100 % for UV_{410} and 92 % for ammonia nitrogen in its stable stage.

Keywords: membrane bioreactor (MBR); powdered activated carbon (PAC); hollow fiber membrane; microfiltration (MF); micro-pollution; organic matter; molecular weight distribution

* Along with the serious water pollution, organic matter has become a major factor restricting conventional water treatment process. Therefore, it is critical to develop a substitute process effective to remove organic matter of various properties in source water, so as to make use of micro-polluted water and cover the increasing water demands. Under such circumstances, the membrane bioreactor (MBR) is developing rapidly owing to its small volume, convenient operation and high efficiency. Nowadays the lower cost and better performance of membranes would make MBR more promising in the field of water treatment. In this bench scale experiment, powdered activated carbon (PAC) was dosed into MBR, so-called PAC-MBR, to decrease the membrane fouling, due to the capability of PAC to adsorb organic matter[1] and ameliorate cake layer[2]. As the efficiency of the process and the quality of the treated water are closely related with organic matter molecular weight (MW), the MW analysis was used to study the removal mechanisms of different MW organic molecules by the PAC-MBR process, which could be divided into three unit processes: microfiltration, PAC adsorption and biological treatment.

1 Materials and methods

1.1 Experimental device of PAC-MBR process

The schematic of the experiment was described in Fig. 1. In the bench scale experiment, one membrane module, provided by Tianjin Motian Membrane Technology Corporation, was submerged into the reactor. It contained hollow fiber membranes, made of polyvinylidene fluoride (PVDF), with a pore size of 0.22 μm and a total surface of 0.5 m^2.

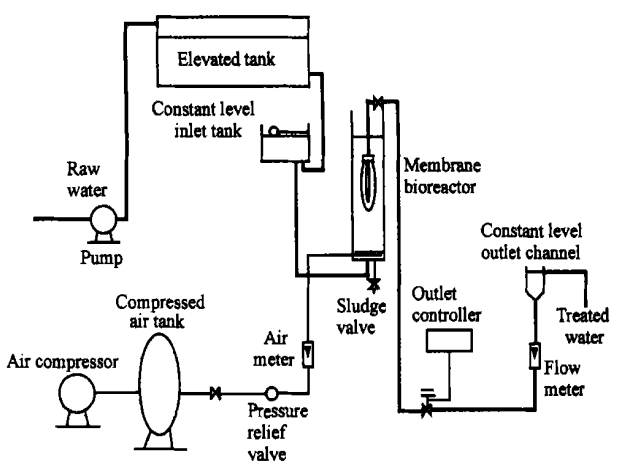

Fig. 1 Schematic diagram of the experimental set-up

The average production capacity was 0.1 m^3/d. During the 163-day operation, raw water, from a lake in Tianjin University, was pumped into an elevated tank every day. It flowed into a constant level inlet tank and

* Accepted date: 2002-03-05.
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* Supported by Tianjin Municipal Science and Technology Commission (No. 013105211).

then to the reactor. Intermittent suction of the treated water was obtained at 8 2' cyclic operations by an outlet controller, then it passed the constant level outlet channel. The driving force for the suction was provided by water levels between the reactor and the outlet channel, which remained constant level. The flow rate of the treated water was adjusted to a constant value by a flow meter. Continuous air diffusion was introduced to the reactor with a ratio of 151: (air to water) through a perforated pipe located at the bottom of the reactor to maintain the flux of membrane and dissolved oxygen required by biomass. PAC was dosed into the reactor at the beginning of the test. The parameters of PAC-MBR operation were adjusted, and could be divided into four stages, which was shown in Tab. 1.

Tab. 1 Operational parameters of PAC-MBR process

Stage	Time/ d	HRT/ h	Sludge discharged/ ($mL \cdot d^{-1}$)	PAC dosage/ ($mg \cdot L^{-1}$)	Total PAC concentration/ ($mg \cdot L^{-1}$)
1	1 —30	4.6	0	0	2000
2	30 —47	2.7	0	0	2000
3	47 —75	2.7	500	7.6	2000
4	75 —163	2.7	500	15.2	4000

1.2 Analytical methods

Removal of organic matter and ammonia nitrogen was particularly discussed in this paper. Organic matter was expressed in terms of COD_{Mn}, UV_{254} and UV_{410}. Samples were tested in accordance with standard methods for water and wastewater analysis[3]. UV_{254} and UV_{410} were measured by a 754 Spectrophotometer with a cell length of 1 cm.

A nitrogen pressured filtration device (SCM cup ultrafiltration system), provided by Membrane Separation Technology Research Center in Shanghai Nuclear Research Institute, was employed in the MW analysis test. It was used to divide soluble organic molecules into 5 sections based on their MWs: < 1k, 1k —4k, 4k —10k, 10k —0.22 μm, and 0.22 μm — 0.45 μm, where 1k referred to 1000 MW cut-off of ultrafiltration and pore size represented the MW section of microfiltration. MF 0.22 μm was used because it was the same as the membrane in the reactor. Samples were filtrated respectively as shown in Fig. 2.

2 Results

2.1 COD_{Mn} removal

COD_{Mn} concentrations of the influent from the inlet water tank, mixed liquor (ML) in reactor (filtrated through filter paper prior to measurement) and treated water (TW) were given in Fig. 3.

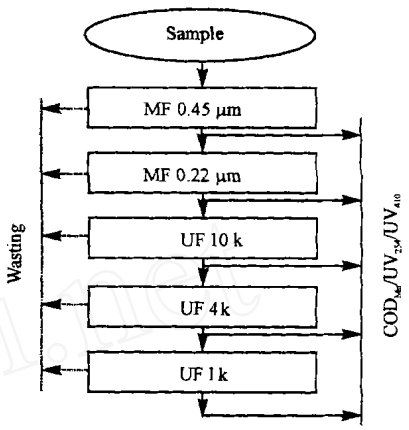

Fig. 2 Diagram of organic MW distribution measurement procedure

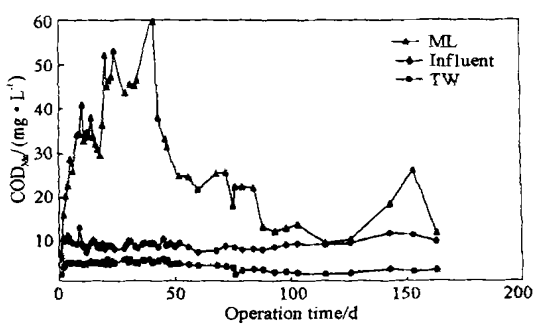

Fig. 3 COD_{Mn} removal by PAC-MBR process

It was shown in Fig. 3 that COD_{Mn} concentration of ML fluctuated greatly. Thus two phases could be identified due to its tendency.

1) COD_{Mn} concentration of ML was increasing. This phase included the period of Stage 1 and Stage 2 (1 —47 d), when two causes would be explained for the increasing. For one reason, the PAC dosed at the beginning reached its adsorption balance and could not remove organic matter any more. At the moment, the function of PAC in the reactor was to slow the flux decline by ameliorating the structure of the cake layer. For the other reason, the biomass in the reactor was not adapted to natural organic matter (NOM), therefore its degradation on NOM was not obvious. As a result, NOM accumulated quickly in the reactor by membrane rejection.

2) COD_{Mn} concentration of ML was decreasing and tended to be steady. This phase included Stage 3 and Stage 4 (50 —163 d). As mentioned in Tab. 1, the operational pa-

rameters were changed obviously when sludge was discharged 500 mL from the sludge valve every day and then fresh PAC was dosed to maintain PAC concentration in the reactor. In this case, COD_{Mn} concentration of ML decreased rapidly after sludge discharging. Considering membrane fouling was greatly related with the organic matter concentration, periodical sludge discharging with PAC dosing was a good way to decrease membrane fouling.

During the operation, COD_{Mn} concentration of the influent was 9.25 mg/L on average, while TW 4.59 mg/L. The removal efficiency decreased in the first phase and then increased in the second, which indicated the relationship between ML and TW. However, this was not in accordance with the discipline that the quality of the effluent was not affected by ML concentration when MBR was used to treat synthetic wastewater[4]. In this experiment, when hardly biodegradable NOM kept piling up in the reactor, the quality of TW and removal efficiency fell. In the first phase COD_{Mn} concentration of TW reached 5—6 mg/L, and removal efficiency about 40 %, while in the second phase, with sludge discharged and PAC compensated, COD_{Mn} concentration of TW went down to 3 mg/L with the removal efficiency of above 70 %.

2.2 UV_{254} removal

The absorbance coefficient at 254 nm (UV_{254}) mainly shows the content of aromatic organic matter. Because of the coherence of UV_{254} with DBPs (THM, etc), UV_{254} absorbance value is an important index to assess the quality of water[5].

As shown in Fig. 4, the tendency of UV_{254} removal was coincident with that of COD_{Mn}. The average UV_{254} was 0.138 for influent, 0.251 for ML and 0.080 for TW. Before PAC was compensated, UV_{254} of TW jumped to 0.124 with the removal efficiency of only 20 %. Fortunately, with PAC dosed, TW turned favorable, with its UV_{254} of about 0.05 and removal efficiency of 70 %.

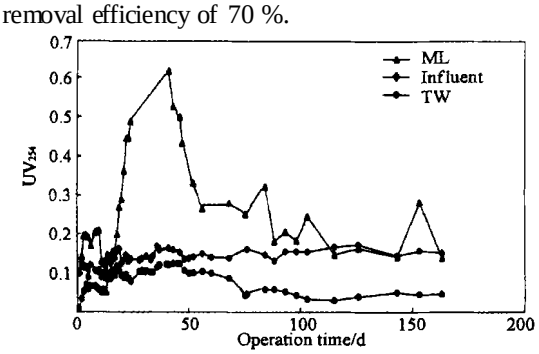

Fig. 4 UV_{254} removal by PAC-MBR process

2.3 UV_{410} removal

Absorbance coefficient at 410 nm (UV_{410}) mainly shows the content of organic matter with relatively large conjugate system, such as humic in NOM, an apparent color forming matter. Therefore UV_{410} absorbance value is in accordance with the color index. Meanwhile it was reported that the decrease in UV_{410} with decreasing molecular size was apparent[6].

As shown in Fig. 5, UV_{410} removal was different from that of COD_{Mn} or UV_{254}. In spite of the increasing UV_{410} of ML, TW was stable. It was estimated that the removal of UV_{410} was primarily attributed to membrane rejection. The removal efficiency was 70 % or so in the first phase, while after fresh PAC was dosed, it reached 100 %, because some permeated organic molecules observed as UV_{410}, whose MWs were relatively low, were adsorbed by PAC.

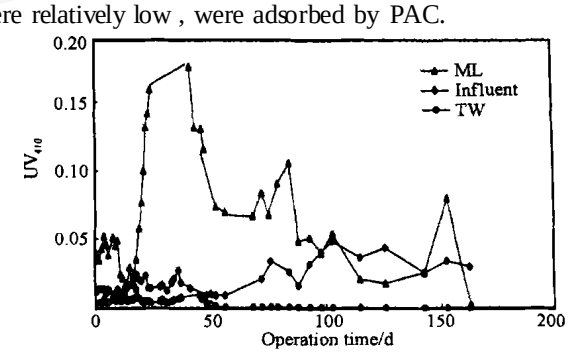

Fig. 5 UV_{410} removal by PAC-MBR process

2.4 Comparison of each removal by PAC-MBR process

As shown in Fig. 6, there were great differences between the patterns of different organic removal.

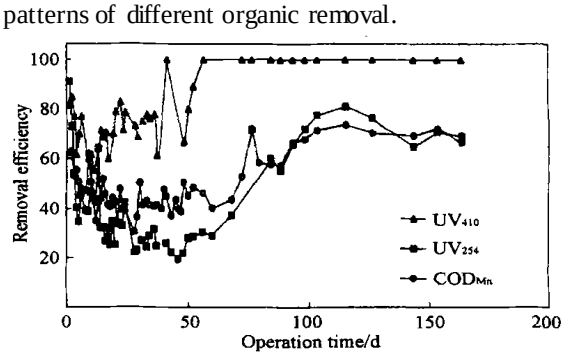

Fig. 6 Comparison of removal by PAC-MBR process

At the beginning, as PAC adsorption capacity saturated, the removal efficiency of COD_{Mn} and UV_{254} fell rapidly and then tended to a constant level, with the removal efficiency of 45 % for COD_{Mn} and 35 % for UV_{254}. After fresh PAC was dosed, the removal efficiency of both indexes began rising; yet the extent was greater for UV_{254}. At the end of Stage 4, when fresh PAC dosage was 15.2 mg/L, the removal effi-

ciency of UV_{254} was above 80 % for some time. These data suggested that PAC dosing could remove organic molecules observed as UV_{254} more than those as COD_{Mn}, which demonstrated the capacity of PAC adsorption was greater for aromatic matter. On the other hand, this discovery would guide process design. For particular raw water of different index, such as UV_{254}/DOC, optimistic proportion of each unit process, including biological treatment and PAC adsorption, should be calculated for the hybrid process.

2.5 Ammonia nitrogen removal

Ammonia nitrogen concentrations of influent and TW were measured and given in Fig. 7.

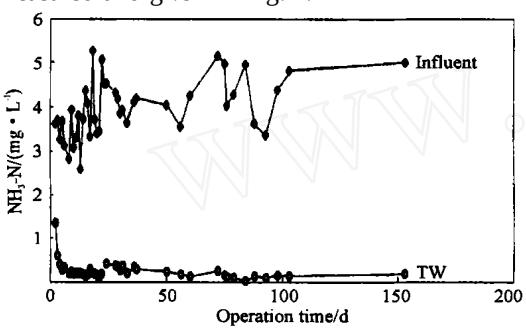

Fig. 7 Ammonia nitrogen removal by PAC-MBR process

Because of long sludge retention time (SRT) and the abundance of dissolved oxygen, it was suitable for nitri-fying bacteria whose generation time was long. Therefore, after the fifth day of operation, ammonia nitrogen was removed more than 90 % by PAC-MBR process. During the processing time, average ammonia nitrogen concentration was 4 mg/L in influent and 0.3 mg/L in TW, and the average removal efficiency was 92 %.

3 MW analysis

In the later period of Stage 4, MW analysis was applied to the organic matter concentrations of the influent, ML and TW. Since the organic matter in TW, observed as UV_{410}, was removed 100 % in Stage 4, only the removal patterns of COD_{Mn} and UV_{254} were discussed as follows.

3.1 COD_{Mn} concentration distribution on each MW section by PAC-MBR process

COD_{Mn} concentration distributions of the influent, ML and TW were given in Fig. 8, where TW1 was obtained before sludge discharging and TW2, 30 min after PAC dosing. Generally, the proportion of low MW (< 1 k) organic matter was increased in TW, which deviated from our prediction. We had expected a better removal of low MW organic molecules by MBR, but it was not the case, mainly because NOM molecules with low MWs in surface water were degradation recalcitrant compounds with a high ratio of UV_{254} to COD_{Mn}. Later in 3.3.1, the surface water biodegradation experiment also gave the reason.

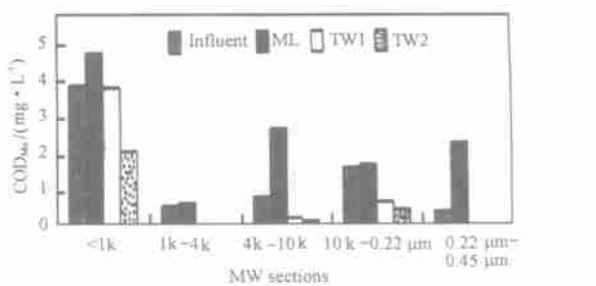

Fig. 8 COD_{Mn} concentration distributions by PAC-MBR process

As shown above, there were distinctive characteristics of COD_{Mn} removal on different MW sections by PAC-MBR process, which were stated as follows.

1) Considering the quality of the surface water used in the experiment, the process should focus on the removal of NOM molecules with MWs < 1k. While NOM molecules were degradation recalcitrant, so it depended on PAC adsorption. The difference between TW1 and TW2 led to the conclusion that PAC contributed a lot. On the other hand, it suggested that NOM might consist of a large amount of soluble microbial product (SMP), which was mostly hydrophobic humic matter. Therefore NOM molecules with MWs < 1k could neither be removed by biomass in a short period of time (HRT = 2.7—4.6 h in the operation), nor blocked by membrane because of their small sizes, thus COD_{Mn} concentration of this section was relatively high.

2) In Fig. 8, COD_{Mn} concentration of ML accumulated mainly on two sections. One was 0.22 μm—0.45 μm section. NOM molecules in this section were relatively large and could be blocked by membrane, however, neither biomass nor PAC removed them effectively, so they kept piling up in the reactor and could only be reduced and controlled by sludge discharging. The other was 4k—10k section. It was reported that PAC adsorption was effective to organic molecules of 0.5k—3k, and could partly remove those of 10k—100k. But to those between them, that were of 3k—10k, the organic molecules were not reduced but increased[5]. Thus such results were not by chance, but included some mecha-

nisms of PAC adsorption and desorption, which deserve further study.

3) Organic molecules in section 1k—4k were removed completely, which could be seen in Fig. 8, with the zero COD_{Mn} concentration of TW1 and TW2. The result was in accordance with the theory that PAC adsorbed organic molecules of 0.5k—3k much more effectively than others.

3.2 UV_{254} on each MW section by PAC-MBR process

The values of UV_{254} absorbance in each section were given in Fig. 9. Compare Fig. 9 with Fig. 8, similarity existed between the two general removal efficiency. In other words, the ratio of TW to the influent tended to be equal. Nevertheless, the removal patterns of COD_{Mn} and UV_{254} distributions were different.

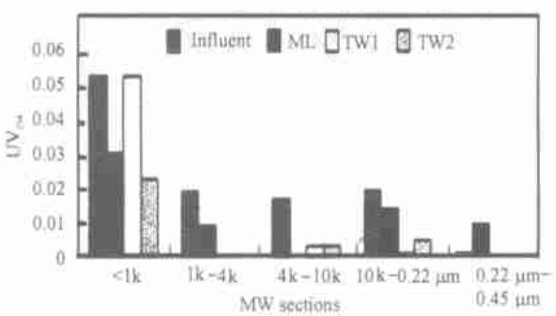

Fig. 9 UV_{254} distributions by PAC-MBR process

Primarily, UV_{254} values on all sections were lower than those of the influent, which was opposite to COD_{Mn} concentrations. This could demonstrate that PAC adsorbed the UV_{254} observed organic molecules more, which tended to be hydrophobic aromatic compounds. Secondarily, on 4k—10k section, the organic molecules observed as UV_{254} did not pile up as those revealed by COD_{Mn} concentration, which could be best shown by the zero UV_{254} value of ML. There might be two reasons for such phenomenon by PAC-MBR process:

1) Biological degradation. Even though organic matter observed as UV_{254} was mostly complicated with phenyl, they could decompose into smaller molecules. This could be seen clearly in Fig. 10. Therefore the removal of NOM on 4k—10k section should be attributed to biodegradation partly.

2) PAC adsorption. As mentioned previously, organic molecules of 4k—10k might be increased by PAC adsorption. It was so for COD_{Mn} concentration in Fig. 8, but it was not the case for UV_{254}. The explanation was that hydrophobic aromatic compounds observed as UV_{254} were more readily adsorbed by PAC. Thus it could be seen, when PAC removal patterns of different MW were discussed, the properties of the adsorpbate should also be considered.

3.3 Comparison of unit and hybrid process removal

3.3.1 MW analysis of biological process

In order to evaluate the biological effect in PAC-MBR process, sludge was incubated in a batch reactor with surface water feed and aeration. One month later, the influent and TW after a retention time of 40 h were measured, as shown in Fig. 10 and Fig. 11.

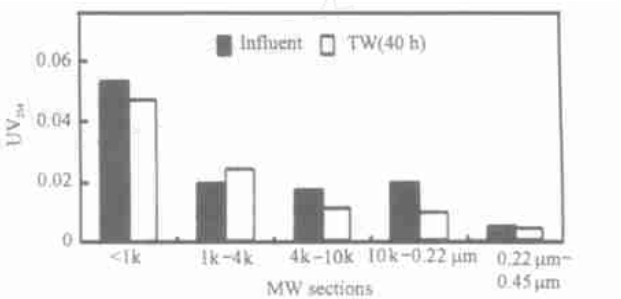

Fig. 10 UV_{254} value distributions by biological process

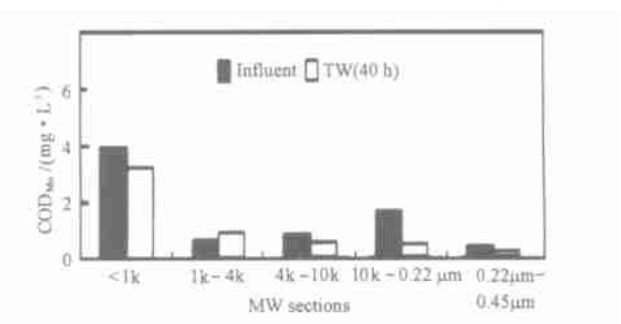

Fig. 11 COD_{Mn} concentration distributions by biological process

The two figures showed similar removal tendency on each section. It should be mentioned that NOM molecules of all sections were removed to some extent by biological process, expect for 1k—4k section. It was surmised that complicated NOM molecules could decompose into relatively simple ones by biodegradation, while the reaction could not go on further, so organic molecules in 1k—4k section increased. However, organic molecules in this section were just what PAC adsorbed best. Therefore, it came to a presumption that the biological process could change organic molecules from high MWs to low MWs, which were more readily adsorbed, thus promoting PAC absorbability by this means.

3.3.2 Promotion of biological process and PAC adsorption

Removal of COD_{Mn} and UV_{254} by three unit processes was given in Fig. 12, where Bio was biological process with a retention time of 40 h, PAC was PAC adsorption with a con-

centration of 20 mg/L and a contact time of 1 h, while Bio + PAC was the integration of them with Bio firstly and PAC subsequently.

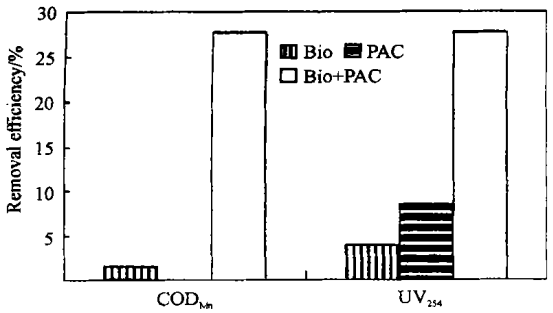

Fig. 12 Removal of COD_{Mn} and UV_{254} by different processes

Fig. 12 shows that neither solely Bio nor PAC could remove organic matter effectively. Furthermore, 20 mg/L PAC adsorption could increase COD_{Mn} concentration slightly, and the removal was shown as zero in Fig. 12. Fortunately, with biological pretreatment, PAC adsorption was greatly enhanced, which demonstrated the presumption mentioned above, that the biological process could promote PAC absorbability by decomposing high MW compounds.

The promotion could also be explained in another way. Since PAC adsorption changed the retention time of soluble organic matter from HRT to SRT, and gave more chance for biological contact and degradation, PAC adsorption could assist the biological process, especially when organic matter was degradation recalcitrant.

4 Conclusions

1) Organic removal efficiency of PAC-MBR process was as high as about 70 % for COD_{Mn} and UV_{254}, and 100 % for UV_{410}, while the average removal of ammonia nitrogen was 92 %. In order to keep the operation stable, it was required to discharge sludge and dose PAC periodically.

2) Organic molecules of treated water from PAC-MBR process were concentrated on < 1k section. They were recalcitrant, while PAC adsorption was effective. Meanwhile, the best removal section by PAC-MBR process was 1k —4k.

3) The biological process might increase organic molecules on 1k —4k section. It was surmised that complicated NOM molecules could decompose into relatively simple ones, while the reaction could not go on further.

4) Biological treatment and PAC adsorption promoted each other in PAC-MBR process. On the one hand, biological degradation could turn high MW organic molecules into lower ones, which were in the best adsorbed section of PAC. On the other hand, PAC adsorption led to longer retention time of soluble organic matter, which might increase the probability of biological removal.

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PAC-MBR 工艺处理微污染地表水的研究

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摘　要:设计了膜生物反应器(MBR)与粉末活性炭(PAC)联合使用的膜组合工艺(PAC-MBR)处理微污染地表水,并用分子量分析方法来考察 PAC-MBR 组合工艺及各单元工艺对有机物的去除效果. 分析结果表明,由于原水中的小分子有机物难生物降解,该工艺出水有机物集中在小于 1k 的分子量区间内,活性炭的投加能显著提高这部分有机物的去除率. 试验证明,PAC-MBR 工艺中生物处理与活性炭吸附互相促进,在稳定运行阶段对 COD_{Mn}、UV_{254}、UV_{410}和氨氮的去除率分别达到 70 %、70 %、100 %和 92 %.

关键词:膜生物反应器;粉末活性炭;中空纤维膜;微滤;微污染;有机物;分子量分布

中图分类号:X703　　**文献标识码**:A　　**文章编号**:1006-4982(2002)03-0159-06