Applicability of Nanofiltration for the Advanced Treatment of Landfill Leachate

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ABSTRACT: Landfill leachates are generated from municipal solid waste landfills under the action of water percolating through the landfilled waste. A treatment system using a combined membrane engineering process was developed to effectively treat the landfill leachate in the Dahanzhuang sanitary landfill (Tianjin, China). The process combines a membrane bioreactor (MBR) and nanofiltration (NF) technology to treat the leachate. The results indicate that the NF system, including the hollow-fiber NF membrane, is an appropriate advanced treatment alternative for landfill leachates. This system provided good removal of chemical oxygen demand and color. The membrane flux renewal reached over 96% after washing with 0.01 mol/L HCl. As a result, the effluent water quality met effluent discharge standards (GB16889-2008). J Appl Polym Sci 116: 2343–2347, 2010

Key words: nanolayers; nanotechnology; polyamides; thin films; waste

INTRODUCTION

Landfills are regarded as efficient, economical and technically sound systems of disposal for solid waste throughout the world. Up to 95% of solid waste generated worldwide is currently disposed of in landfills.[1–3] After landfilling, leachate generation is an unavoidable process in landfills. *Leachates* are the aqueous effluents generated as a consequence of rainwater percolation through wastes, biochemical processes in waste cells, and the inherent water content of the wastes themselves.[4–6] Depending on the maturity, age, and biochemical reactions occurring in the landfill, the characteristics of a leachate vary significantly in terms of organics, ammonia nitrogen, heavy metals, dissolved solids, chemical oxygen demand (COD_{Cr}), and color.[7] As a result, the treatment of landfill leachate to comply with effluent discharge standards is often complicated and expensive. Usually, a combination of physical, chemical, and biological methods is used for landfill leachate treatment because it is difficult to obtain satisfactory treatment efficiencies by either of these methods alone. A reported case[8] showed that the combined treatment technology could improve the effluent quality and minimize the residue generated at a lower treatment cost compared to the individual treatment methods.

In recent years, many new treatment methods for landfill leachate have been developed,[9–11] among which nanofiltration (NF) technology showed advantages in the removal of dissolved matters.[12] NF seems to be one of the most promising and efficient methods among processes for landfill leachate treatment. The advantage of using an NF membrane is that it requires lower operating pressures (between 350 and 1000 kPa), has higher fluxes than reverse osmosis (RO) membranes, and has better retention than an ultrafiltration (UF) membrane.[13]

In this study, NF advanced treatment of the leachate for the Dahanzhuang sanitary landfill (Tianjin, China) was investigated with the membrane characteristics given in Table I, together with consent discharge limits for the leachate to a local sewer in China. Although MBR pretreatment is a very effective treatment method for high-strength leachates, additional posttreatment is needed to satisfy discharge limits.

The major objective of this study was to investigate the effects of NF on the advanced treatment efficiency of landfill leachate. The landfill leachate was pretreated by a membrane bioreactor (MBR) with an air-lift bioreactor and an UF system.

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TABLE I
Properties of the Membranes Used

Item	UF membrane	NF membrane
Membrane material	PVDF	Polyamide/PSF
Membrane type	Tubular	Hollow fiber
Inside diameter/outside diameter of the membrane (mm)	12/15	0.75/1.1
Module length (mm)	1,000	500
Number of fibers	10	102
Inside diameter of the modules (mm)	45	30
Module size (m^2)	0.75	0.24
Flow type	Inside out	Inside out
Pressure drop across the membrane (MPa)	0.1	0.7
Temperature (°C)	25	25
Water flux (L m^{-2} h^{-1})	1,000	40
MWCO	100,000	200
Rejection to 0.5 g/L NaCl (%)	—	13.0
Rejection to 1.0 g/L $MgSO_4$ (%)	—	98.7

EXPERIMENTAL

Landfill leachate

The raw landfill leachate was collected from an equalization storage tank of the Dahanzhuang sanitary landfill (Tianjin, China), which was built in 2002 and was put into service in January 2005. It occupies an area of 10 ha, with a total filling space of 8.5×10^6 m^3 and a disposal capacity of 1800 ton/day. The leachate originated from the Dahanzhuang landfill, which receives primarily domestic and some industrial wastes. The produced leachate was collected in an artificial pond, located at the lowest side of the landfill.

Membranes

Two different types of membranes were used in the experiments (UF and NF membranes). The specifications of the membranes are given in Table I. The tubular UF modules were obtained from MOTIMO Co., China.

The NF membranes were prepared through an interfacial polymerization technique described in the literature.[14,15] The general method developed in this study involved the reaction of a diamine with an acyl chloride on the internal surface of a porous polysulfone (PSF) support membrane (supplied by MOTIMO, with a 1.1-mm pore size by the bubble point method, 84% void volume, and 84 mm thickness), which was fabricated by a wet-spinning process.[16] Nascent membrane samples were washed with acetone, with two washes of 3 min each, before the initial mass was determined. A diamine was first deposited on the internal membrane surface by drying from water, and the membrane was then exposed to 100 mL of 0.5 g/L trimesoyl chloride *n*-heptane solution for 15 s, which resulted in the formation of an ultrathin polyamide film over the PSF support. The resulting composite membranes were washed thoroughly with deionized water and stored in deionized-water-filled lightproof containers at 5°C. The diamine used was a 2 g/L aqueous solution of piperazine. The rejection performance of the NF modules were characterized by rejection and water flux to aqueous inorganic salts solutions, such as aqueous NaCl and $MgSO_4$ solutions.[17]

The structure of the composite NF membrane was characterized by scanning electron microscopy (SEM). To prevent the destruction of the structure of the cross sections of the hollow fibers, membrane samples for SEM were first immersed in liquid nitrogen, fractured, and then sputtered with metallic gold to obtain an adequate contrast of the membrane fracture. A Cambridge S-250 field emission scanning electron microscope was used to investigate the morphology of the hollow-fiber membranes.

Experimental procedure and analysis

All experiments were performed at the Dahanzhuang sanitary landfill in October 2008. Figure 1 shows a schematic drawing of the experimental system used in this study. The leachate treatment system was composed of an MBR with tubular-type membranes and an NF process with a hollow-fiber-type membrane. The tubular membranes had a diameter of about 5–15 mm. Because of the size of the membrane surface, the plugging of the tubular membranes was not likely to occur.

MBR unit

The MBR unit was composed of a bioreactor with a 1000-L working volume and two membrane modules. The membrane modules were made of 0.10-μm tubular membranes of poly(vinylidene fluoride) (PVDF; MOTIMO). Each membrane module with an area of 0.5 m^2 was placed outside the bioreactor and connected to the bioreactor by two pipes with valves. The reactor was filled up with granular sludge from an industrial wastewater treatment

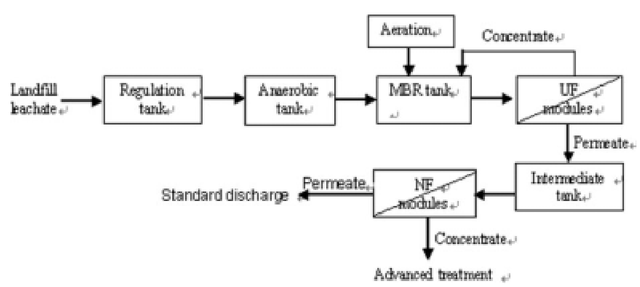

Figure 1 Flow diagram of the leachate treatment system.

TABLE II
Characteristics of the Raw Leachate and MBR Effluent

	Color	COD_{Cr} (mg/L)	NH_4^+—N (mg/L)	Conductivity (mS/cm)
Raw leachate	Black	4670–6700	820–960	14.9–15.3
MBR effluent	Brown	568–850	0–2	0.78–11.4
GB16889-2008[a]	20 (10) times	100 (60)	25 (8)	—

[a] Standard for Pollution Control on the Landfill Site of Municipal Solid Waste. The data shown in the bracket is the first-class standard.

plant and an increasing percentage of leachate. The biological treatment of the leachate under anaerobic conditions was conducted with anaerobic granular sludge at a concentration of 10 g/L. Experiments were performed at a temperature of 35°C. Landfill leachate was collected in the regulation tank and transferred to the anaerobic tank, then the MBR tank, and the first-stage UF modules unit. A permeate of the first stage was fed to the second-stage NF units for polishing, and the permeate from the second stage was neutralized and sterilized before disposal in the Paixian River.

Crossflow NF experiment

The effluent from the anaerobic bioreactor was post-treated with the NF unit. A NF hollow-fiber membrane module (homemade) was adopted for this study. It had a molecular weight cutoff (MWCO) of 200 g/mol and an active surface of 0.24 m^2. The NF experiments were performed in the temperate range 11.5–16°C and 0.7 MPa. The total volume of the influent leachate was 15,000 L for the NF concentration process.

Chemical analysis

All chemical analyses were done within 3 days after sampling. The leachate samples were analyzed for conductivity (MC226 conductivity meter, Zurich, Switzerland), color (color was measured in duplicate with the 2120 C spectrophotometric method), and COD_{Cr} (measured with the titrimetric method after dichromate closed reflux). Kjeldahl nitrogen was determined by an autoanalyzer (Lachate Quickchem AE automated ion analyzer dual-channel system C/N 2200-100, Ontario, Canada) after semi-micro-Kjeldahl digestion. The analytical methods used were in accordance with standard methods [The American Public Health Association(APHA), 1985].

RESULTS AND DISCUSSION

Pretreatment of the landfill leachate

The leachate originated from the Dahanzhuang sanitary landfill in Tianjin (China), which receives primarily domestic and some industrial wastes. The main physiochemical characteristics of the raw leachate and MBR effluent used during the experiment are shown in Table II. The characteristics of the leachate used in this study (Table II) reflected a relatively young landfill. The initial COD_{Cr} and NH_4^+—N concentrations were in the ranges 4670–6700 and 820–960 mg/L, respectively. The NH_4^+—N concentration was insignificant in the produce water during the MBR operation. Despite high NH_4^+—N removal efficiency in the MBR, COD_{Cr} removal was not as satisfactory as that of NH_4^+—N removal. In addition, improvements in the MBR in the color and conductivity were not obvious. Therefore, when the MBR treatments were followed independently, the leachate still did not meet with the effluent discharge standards (GB16889-2008).

COD_{Cr} removal in the NF process

The average effluent COD_{Cr} from MBR was at a level of 800 mg/L with a rate of 87% removal, and then, the effluent was transferred to NF (Fig. 2). Because of the inhibition of the activity of microorganisms by heavy metals and because some organics may be present in leachates, the biological oxygen demand (BOD) parameter gives suppressed results and therefore, leachates are more often described by their COD_{Cr}. Dissolved nonbiodegradable organic matters and negatively charged nitrified compounds

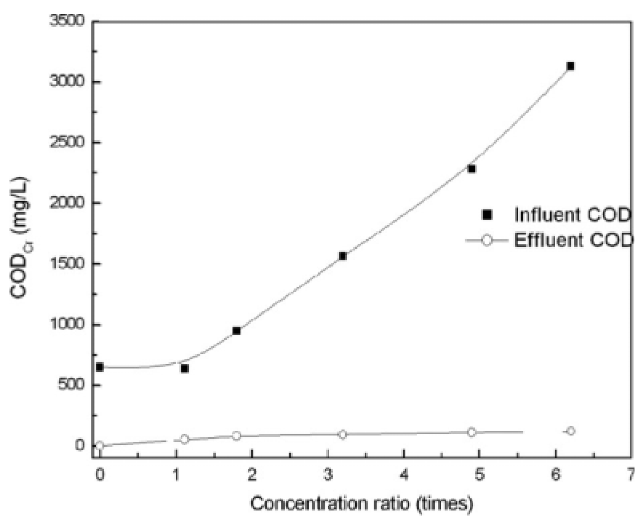

Figure 2 COD_{Cr} removal efficiencies during the NF concentration process.

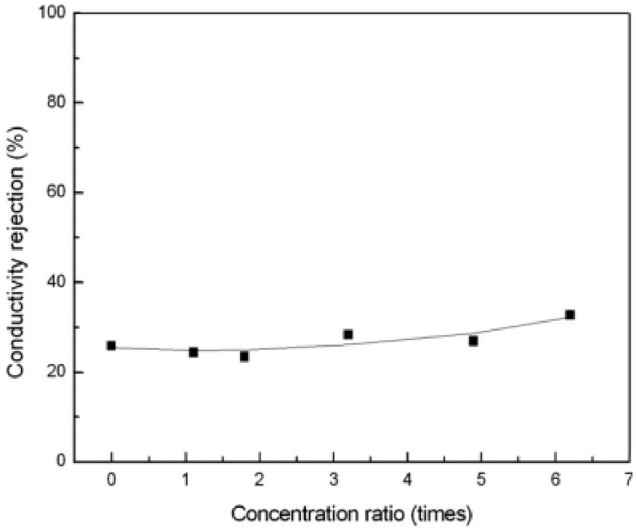

Figure 3 Color removal efficiencies during the NF concentration process.

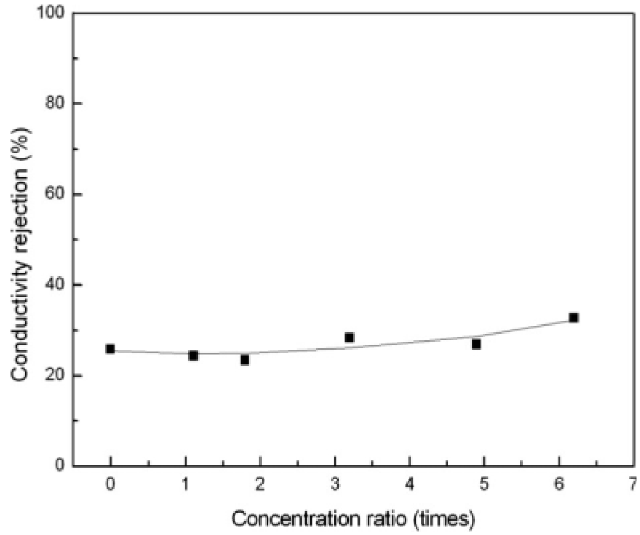

Figure 4 Conductivity removal efficiencies during the NF concentration process.

are effectively removed by subsequent NF membranes. The effect of concentration ratios on COD_{Cr} was observed to investigate the COD_{Cr} removal performance in the NF process (see Fig. 2). As shown in Figure 2, the influent COD_{Cr} was between 630 and 3140 mg/L. This concentration level of COD_{Cr} decreased to approximately 51–120 mg/L in the permeate. Excellent COD_{Cr} removals were obtained with NF membrane.

Color removal in the NF process

Figure 3 shows the color removal by the NF process. Similar to COD_{Cr} removal, almost all of the color present in the effluent of the MBR was removed by the NF treatment. The color met with the first-class discharge standard of the National Municipal Waste Sanitary Landfill Pollution Control Standard (GB16889-2008, China).

Conductivity removal in the NF process

Figure 4 shows that with increasing concentration ratio in the investigated range, the conductivity rejection increased slightly. The rejection value was lower than 35%. Kurniawan et al.[18] investigated the composition and characteristics of raw landfill leachates of different ages.[18] From their research, the concentration of heavy metals was lower than 2 mg/L in a stabilized leachate because of decomposition in the landfill. In similar research, the data showed that the leached fractions of heavy metals often remained lower than 10%, either for the coprecipitated organic matter and/or the temporary hardness (Ca^{2+} and Mg^{2+}).[19] Typically, NF membranes do not have a high rejection of monovalent ions, but the rejection of divalent ions can be significant. Therefore, the reduction of conductivity was not obvious in the NF process and could be attributed to the lower heavy-metal concentration.

Permeate flux in the NF process

Figure 5 presents variations of the water fluxes measured over 10 days. During the sampling period, the experimental temperature was low (11.5–16°C). As a result of this and the concentration polarization, the permeate flux was tremendously lower than the initial flux (shown in Table I). A reduction in the flux with time during the initial 6 days was attributed to NF membrane fouling. The results show that the use of 0.01 mol/L HCl as a detergent (on the 6th day) was a better method and with

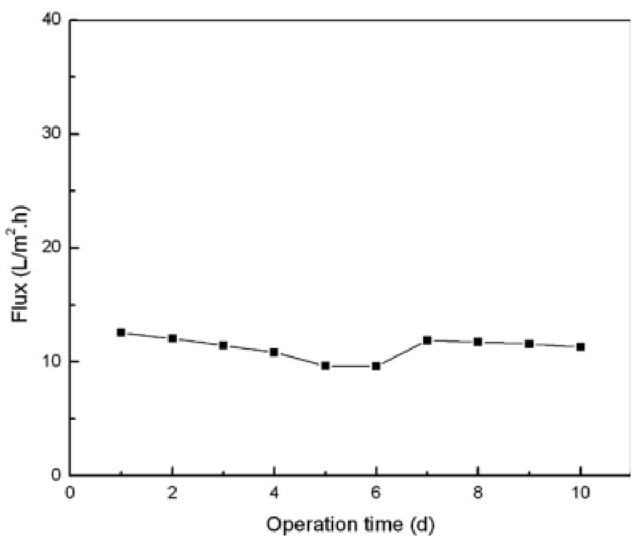

Figure 5 Flux variation of NF effluents over 10 days from October 11, 2008 to October 21, 2008.

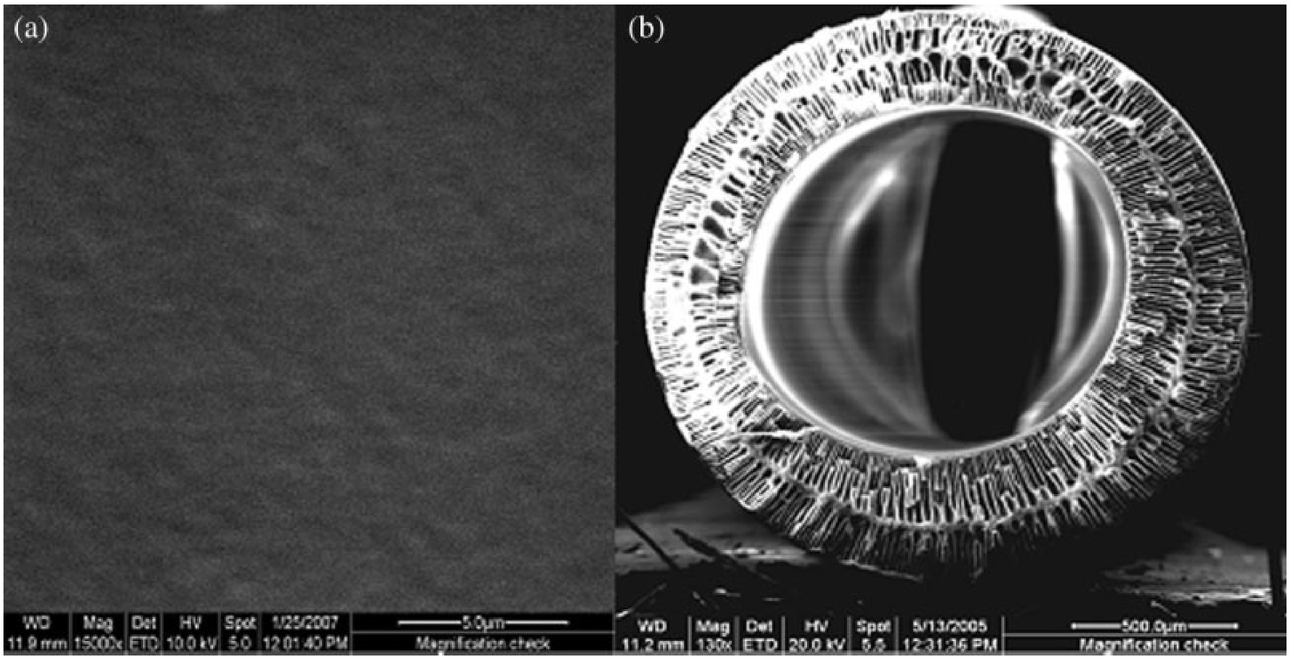

Figure 6 SEM micrographs of the (a) inner surface and (b) cross-section views of hollow-fiber-type NF membranes.

which the membrane flux renewal reached over 96% on the 7th day.

SEM analysis of the NF membranes

The inner surface and cross-sectional structures of the NF membranes were observed through a scanning electron microscope. As shown in Figure 6, morphological studies of the inner surface of the hollow fiber were conducted by SEM and revealed an extremely flat film. From SEM micrography of the cross section of the membrane, we observed that the hollow-fiber membrane had a double fingerlike structure (macrovoid) in cross section. We concluded that the section morphology was more similar to the support hollow fiber because the polyamide layer was an ultrathin film.

CONCLUSIONS

Our integrated method of treatment consisted of an MBR, and NF was used to treat landfill leachate in the Dahanzhuang sanitary landfill (Tianjin, China). The quality of the effluent from the MBR was not appropriate for discharging into receiving waters and required additional advanced treatment regarding polishing purposes. So, an NF process was adopted to concentrate the MBR effluent. The permeates obtained were clear and colorless. The results obtained very clearly confirmed that NF is a very efficient treatment in the removal of organic and inorganic pollution. The results of the second-stage NF concentration treatment applied to the MBR effluents clearly demonstrated that the performance of COD_{Cr} and color removal from the leachate were excellent in the NF process. The advanced treatment of the leachate with NF seemed to be an economical and viable solution for the minimization of environmental risks. The high-quality treated water met well the first-class discharge standards of the National Municipal Waste Sanitary Landfill Pollution Control Standard.

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