Treatment of Landfill Leachate RO Concentrate by VMD

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***Abstract*—Reverse osmosis (RO) concentrate has been one of the concerned environmental pollution since the RO membrane is widely applied. RO concentrate has a dramatic impact on the useful life of landfill, surrounding soil and ground water. Thus, the RO concentrate is also urgent to be solved. In this research, we firstly explored the characteristics of vacuum membrane distillation (VMD) by monitoring the membrane flux after controlling for three variables: inflow temperature, inflow flux and vacuum degree downstream and found out the optimum operating conditions. Then we further tracked the running instances of the system by testing the membrane flux and the effluent pH, conductivity, TOC and COD at two different temperature. As for the membrane fouling and wetting, a SEM/EDX analysis was conducted and an efficient solution was given. Finally, we found out that when the vacuum pressure is set at 0.08Mpa, inflow flux is set at 200L/h and at 75℃ or 80℃, we can get a relatively ideal membrane flux. The deterioration of effluent quality and membrane fouling happened in the VMD experiment at 80℃ faster than at 75℃ and "soaking with alkali, acid and tap water + drying" process is available to function recovery.**

Keywords-reverse osmosis concentrate; vacuum membrane distillation; membrane fouling

I. INTRODUCTION

Since the leachate discharge standards were improved in China after the publication of <Standards for pollution control on the landfill site of municipal solid waste> (GB16889-2008) in 2008, RO membrane have been more widely applied. If most concerning matter using the RO membrane is the concentrate, which is with no biodegradability, high salinity and high COD have been released into the environment, its persistent organic and inorganic pollutants will cause the pollution of solids, surface water and ocean and its excessive total suspended solids (TSS) has a negative effect on activated sludge growth. However, there is no perfect treatment for the membrane concentrate so far.In our study, we chose an efficient technology--vacuum membrane distillation (VMD) as the solution for RO concentrate reduction and a multivariable-control experiment was conducted to investigate the characteristics of RO concentrate. To further verify our consequences, we adopted the RO membrane concentrate from Liming landfill in Shanghai as our experiment subject.

II. MATERIALS AND METHODS

A. Materials

The characteristics of the RO concentrate from Liming landfill are listed in Table I

TABLE I. CHARACTERISTICS OF THE RO CONCENTRATE QUALITY

Index	Value	Index	Value
pH	7.23	Na (mg/L)	3914
Conductivity(μS/cm)	51400	Mg (mg/L)	498
BOD_5 (mg/L)	365	Al (mg/L)	14.50
COD_{Cr} (mg/L)	7450	Zn (mg/L)	0.80
TOC (mg/L)	1820	Fe (mg/L)	2.89
NH_3-N (mg/L)	1580	Mn (mg/L)	1.17
TN (mg/L)	4575	Cu (mg/L)	0.14
TP (mg/L)	23	As (mg/L)	0.52
Cl^- (mg/L)	6430	Ni (mg/L)	0.37
NO_3^- (mg/L)	5620	Cr (mg/L)	0.32
NO_2^- (mg/L)	5388	Cd (mg/L)	Undetected
SO_4^{2-} (mg/L)	453	Pb (mg/L)	0.13
K (mg/L)	3783	Be (mg/L)	Undetected
Ca (mg/L)	552	Ba (mg/L)	0.18

B. Equipment of VMD

The equipment our research adopted is shown in Fig.1.

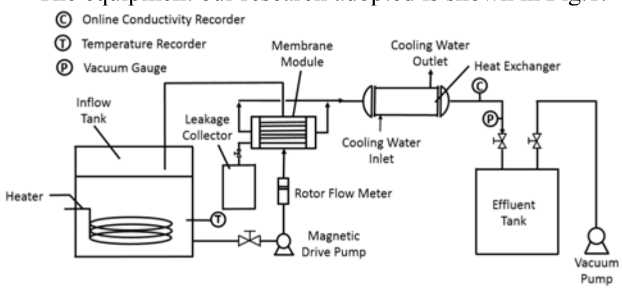

Figure 1. The VMD's Equipment

1) Main Devices of VMD system

TABLE II. DEVICES' DETAILED INFORMATIONS

Device	Model	Materials&Index
Inflow Tank	Customized	Polypropylene (PP) V=25L
Effluent Tank	Customized	PP V=6L
Leakage Collector	Customized	PP V=5L
Heater	Customized	Titanium P=1.5kW
Heat Exchanger	Customized	TitaniumEffective Area=0.5m^2
Magnetic Drive Pump	MP-20R	Q=22L/min H=2m P=20W
Rotor Flow Meter	LZB-10	Q:25~250L/h
Circulating water vacuum pump	SHB-B	Max Vacuum Degree=0.1Mpa
temperature patrolinstrument	XSL16\A-HV0	Error=±0.2%F.S
Online Conductivity Recorder	CCT-5320	Max value= 1.0×10^4 μS/cm
Vacuum Gauge	--	-0.1~0Mpa

2) Membrane Modules

TABLE III. PARAMETERS OF MEMBRANE MODULES

Quantity of Fiber	Effective Length	Effective Width	Effective Height	Effective Area
450	75mm	75mm	30mm	0.1m^2
Material	Width	Inner Diameter	Outer Diameter	Average Aperture
PP	220μm	610μm	1050μm	0.2μm

The PPHFM are arranged parallel in the housing, with both ends stuck using epoxy resin sealant. The inlet and outlet of the feed liquid is perpendicular to the membrane, which is also called "cross-flow". Besides, when large amounts of liquid accumulate due to membrane wetting, it will run into the leakage collector.

C. Methods

1) Methods of Water Quality Monitoring

The main water quality indexes we monitored and their analysis methods are listed in Table IV

TABLE IV. ANALYSIS METHOD AND DEVICES

Index	Method	Device
pH	Glass Electrode Method	HACH HQd portable pH analyzer
Conductivity	Electrode Method	HACH HQd portable conductivity analyzer
COD_{Cr}	Rapid Digested Spectrophotometry Method	HACH DR-3900 spectrophotometry HACH DRB200 elimination reactor
BOD_5	Pressure Transducer Method	HACH BODTrak
TOC	Non-dispersive Infrared Absorption Method	Shimadzu TOC-L CPH/CPN

2) Methods of Test Items

To analyze the membrane fouling, SEM/EDX analysis was conducted to the hollow fiber membrane using the FEI Nano SEM 430 Ultrahigh resolution thermal field emission SEM and X-ray energy dispersive spectrometer.

III. RESULTS AND DISCUSSION

A. Characteristics of VMD

In this chapter, tap water were used to investigate how the operational factors influence the VMD process so as to understand the influence regularity of the operational index on membrane flux and prepare for the further study on the actual RO membrane concentrate. The temperature grades were designed as follows: 70℃, 75℃, 80℃, 85℃, the flux grades were: 50L/h, 100L/h, 150L/h, 200L/h, while the vacuum degree grades were: 0.08MPa, 0.07 MPa, 0.06 MPa, 0.05 MPa, 0.04 MPa

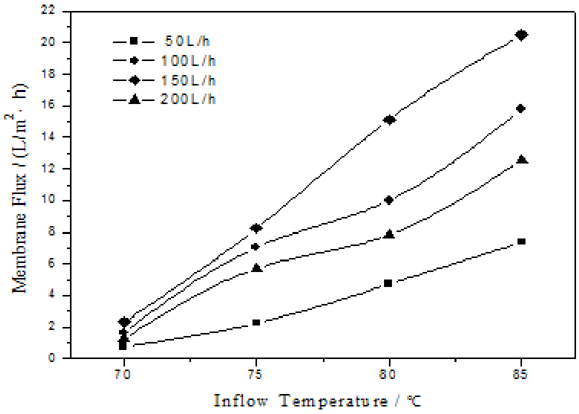

Figure 2. Influence of Inflow Temperature on Membrane Flux with Different Inflow Flux

1) The Influence of Inflow Temperature (Under the condition of 0.08MPa vacuum degree)

As shown in figure 2 above, the membrane flux had a correspondingly increased with the inflow temperature under definite system vacuum pressure and inflow flux. The rising saturated vapor pressure with temperature, causing the greater force membrane distillation driven by, finally came to the adding membrane flux. Concerned the heating as the main source of energy consumption, the cost was also taken in consideration when we decided the operational temperature in our experiments.

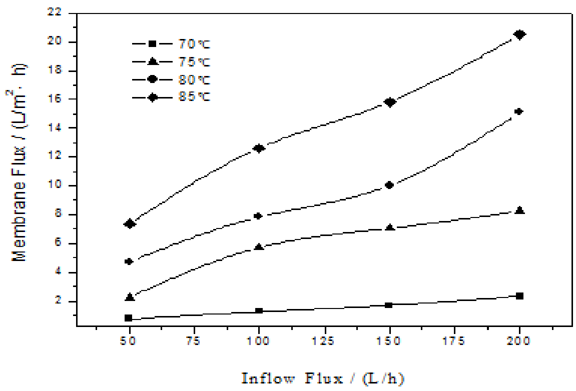

Figure 3. Influence of Inflow Flux on Membrane Flux with Different Inflow Temperature

2) The Influence of Inflow Flux (Under the condition of 0.08MPa vacuum degree)

Figure 3 showed that the membrane flux increased when inflow flux increased and inflow temperature influenced growth ratio of membrane flux. With the inflow flux increased, the turbulence of fluids will rose, and then temperature polarization and concentration polarization weakened. Theoretically, latent heat of vaporization will grow when there is larger membrane flux, which makes the surface temperature of membrane lower, therefore the temperature polarization will be more significant even at a lower temperature. So the membrane flux depends more on turbulence than temperature.

There are some research reveals that the membrane flux will gradually tend to be steady with the growth of turbulence [1,2]. In fact, to increase the inflow flux has a less influence on temperature and concentration boundary layers when the turbulence reached a certain degree.

3) The Influence of Vacuum Degree Downstream(at 85 ℃ and 200L/m^2•h inflow flux)

The membrane flux held steady just under 3L/m^2·h when vacuum degree was below 0.06Mpa under definite temperature and inflow flux, and then the membrane flux made a linear increase along with the increment of vacuum pressure (see Graph 1.3). The transmembrane flux is proportional to vapor pressure difference (VPD) of water, expressed mathematically in formula 1. When the temperature is constant in a VMD system, vacuum degree downstream become the determinant factor of VPD, explaining the linear increase of membrane flux with vacuum degree. However, when the vacuum degree is relatively low, its influence on mass transfer resistance is less than other factors, such as temperature difference, accounting for the flat part of the curve.

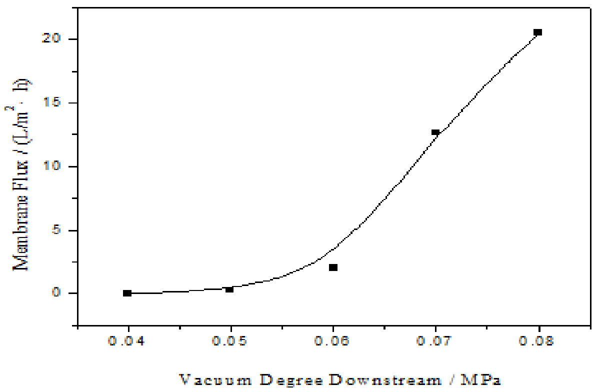

Figure 4. Influence of Vacuum Degree Downstream on Membrane Flux

$$J = K_m \times \Delta p \quad (1)$$

J :Transmembrane flux, K_m : Membrane Distillation Coefficient (MDC), ΔP: VPD of water[3]

Whereas, a higher vacuum degree is by no means better, when the vacuum degree is even higher than the LEP, the hydrophobic membrane channel get wetting and the percolation phenomena occur. 0.08Mpa is the highest vacuum degree we can stably implement and ensure of lower effluent conductivity so far, therefore, we chose 0.08Mpa as a fixed parameter to explore further about membrane distillation process.

B. Study on the RO Concentrate treated by VMD

According tothe prior study, the vacuum pressure is set at 0.08Mpa, inflow flux is set at 200L/h and the temperature is 75℃ or 80℃ are relatively ideal conditions. Therefore, the following experiment was carried out under these conditions. Entering the carbonate balance principle of natural water [4], the main speciation of carbonate was HCO_3^- and H_2CO_3/CO_2 at pH below 6.3. In process of VMD, CO_2dispersed when heating, making the H_2CO_3/CO_2 convert to HCO_3^-/CO_3^{2-}. Using2mol•L^{-1} concentration of HClto adjust pH aimed to avoid $CaCO_3$ sediment, the most common inorganic pollutant of membrane. The records of effluent conductivity was constantly proceeded using online conductivity recorder. While the membrane flux was measured by effluent volume every two hours and the pH, COD_{Cr} and TOC were recorded..

1) VMD Experiment under the Condition of 75 ℃

From figure 5, the conductivity maintained in lower level (between 250 and 550μS/cm), compared to the original 51440μS/cm, so the desalination ratio reached up to 98.9%~99.5% during the first 2 hours after running the system. But then,the leakage increased and showed similar conductivity to the inflow. It's very likely that the RO membrane might be perforated. After restarting the vacuum pump, conductivity moved up sharply to 2494μS/cm, 848μS/cm and 1729μS/cm, and then recovered to the normal level (below 500μS/cm) in 0.5h. However the effluent quality grew significantly worse 10h later, the conductivity even rose up beyond 9000μS/cm and the average leakage reached to 1.5L/h. This tendency was controlled after the system ran for 14h and the effluent conductivity reduced to a stable level (below 300μS/cm).

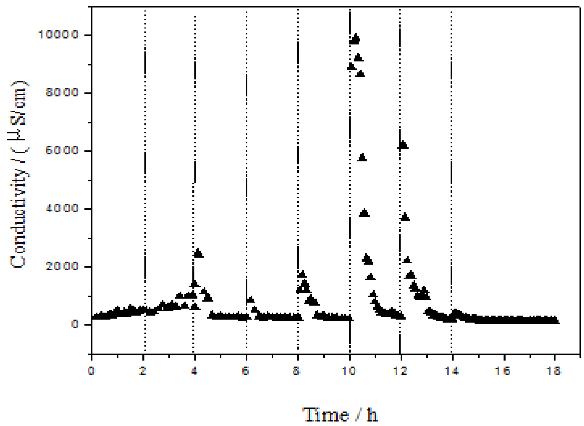

Figure 5. Real-time Recording of effluent Conductivity at temperature 75℃

Figure 6 shows characteristics of effluent: pH, COD and

TOC every two hours (Sincethe effluent volume decreased, we changed the interval of sampling to 4h for the last time). During the first 10h, COD retained its value between 120 and 180mg/L, and TOC was 25~30mg/L, which revealed that remove rate reached 97% above. Then the COD value dropped from 545mg/L to below 200mg/L. The RO concentration contained numerous volatile acids. Their rapid volatilization during the first 6h and dissolution in effluent made the effluent pH go up from 2.84 to 8.7 and finally reached a steady weakly alkaline or neutral state.

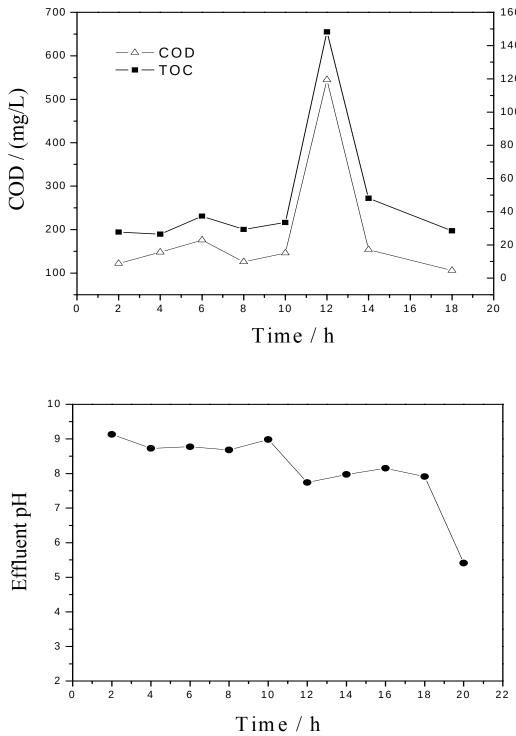

Figure 6. Effluent Characteristics of pH, COD and TOC

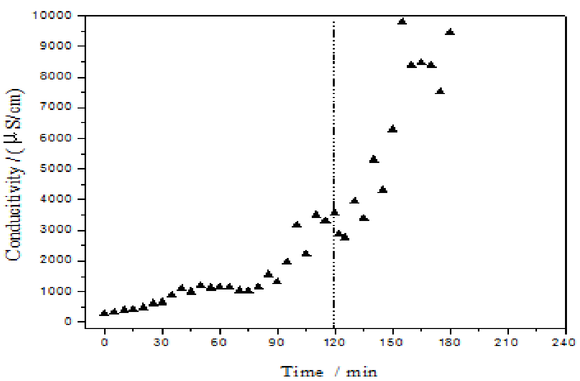

Figure 7. Real-time Recording of effluent Conductivity at temperature 80℃

2) VMD Experiment under the Condition of 80 ℃

Only during the first 90min, the effluent conductivity kept its value below 1000 μS/cm, then effluent quality worsened and its conductivity rose beyond the upper limit of online conductivity recorder and serious leakage happened. The conductivity, COD and TOC increased dramatically in 2 hours. The membrane pollution and concentration polarization led to the 30% drop in membrane flux compared with the tap water experiment under the same conditions (see Table V)

TABLE V. CHARACTERISTICS OF EFFLUENT SAMPLE

Sample Time	Membrane flux (L/m^2•h)	conductivity (μS/cm)	COD (mg/L)	TOC (mg/L)	pH
2h	10.5	1574	272	63	3.47
4h	10.75	9090	1172	363	5.01

The membrane fouling, wetting and deterioration happened in shorter time. Firstly, the rising temperature made the membrane flux increase, and more serious concentration polarization accelerated the sediment of organic and inorganic pollutants[5]. Secondly, the colloids that were not removed by microfiltration were to blame for the membrane contamination. Big condensates combined by colloids deposited on the surface of membrane and higher temperature accelerated this process[6]. Thirdly, the temperature-sensitive organics might volatilized when the temperature rose and then when it got through the membrane channels, the organics condensed because of heat exchange, which weakened the hydrophobic and speeded up the wetting.

C. Membrane Fouling Analysis

1) Principle Components Analysis of Fouled Membrane

The SEM analysis revealed that the external surface of polluted membrane was covered by numerous granular and massive sediments while the internal was covered by plentiful flaky sediments. Table VI showed that the main elements on the external surface of polluted membrane were element C, O, Ca, and Na, Cl, Fe, Mg, Si were detected. The content of oxygen increased due to the oxy-organics and inorganic salts. Since sulfur wasn't detected, the $CaSO_4$ was ruled out from the possible staples and the $CaCO_3$ was also excluded because of hydrolysis pretreatment. The RO concentrate was rich in humic acid (HA) and fulvic acid (FA)[7], whose molecular chains contained carboxyl, phenolic hydroxyl groups and other oxygenic groups[8]. This made it possible for HA to ion exchange or chelate, so the carbon chains of HA winded. The increase of hydrophobic and winded carbon chains made the HA adsorption much easier. Therefore, it's well ground that gelatinous sediments chelated by HA and calcium ions.

TABLE VI. EDXQUANTITATIVE ANALYSIS OF INTERNAL AND EXTERNAL SURFACE OF POLLUTED MEMBRANE

Items	External Surface					Internal Surface			
	1	2	3	4	5	1	2	3	4
C(w%)	17.49	18.62	--	20.06	18.59	73.61	79.88	97.74	73.71
O(w%)	47.13	54.48	60.72	40.77	53.43	26.39	20.12	2.26	26.29
Na(w%)	--	--	--	11.29	--	--	--	--	--
Mg(w%)	--	1.23	--	--	--	--	--	--	--
Ca(w%)	--	25.48	39.28	4.82	27.97	--	--	--	--
Fe(w%)	--	--	--	11.04	--	--	--	--	--
Si(w%)	--	--	--	2.36	--	--	--	--	--
Cl(w%)	--	--	--	9.65	--	--	--	--	--

2) The Cleaning and Regeneration of Membrane

We adopted "20min 0.05mol•L^{-1}NaOH +20min 0.05mol•L^{-1} HCl+30min tap water" process toclean the membrane. Its conductivity and membrane flux at 85℃ turned out to be 40μS/cm, 17.2 L/m^2•h after (98μS/cm,15.6 L/m^2•h before), which meant using acid and alkali didn't help. Then we used "0.1mol•L^{-1} NaOH soaking for 5h，0.1mol•L^{-1} HCl soaking for 5h，tap water soaking for 5h，drier at temperature 60℃" process and repeated. The average conductivity declined to 25μS/cm while the flux was 18.5 L/m^2•h. No leakage showed it was available for function recovery.

IV. CONCLUSIONS

Under current conditions, higher inflow temperature, greater vacuum pressure and larger flux will increase the membrane flux.In the VMD experiment at 75℃, the wetting and leakage occurred in 4 hours and got worse over time, led to deterioration of effluent quality and decline of effluent flux. In the VMD experiment at 80℃, the membrane fouling and wetting worsened and the deterioration happened within 4 hours. The membrane fouling and wetting were attribute to organic and inorganic sediment. The LEP decreased due to highly concentrated organic matters, so the wetting accerlarated. The SEM/EDX analysis indicated that the main contaminants on the external surface are gelatinous sediments while internal contaminants are oxy-organics."Soaking with acid and alkali + drying" process is the most effective for function recovry

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