

# Recovery of humic substances from landfill leachate via 2500 Da ultrafiltration membrane

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## Abstract

Landfill leachate management is getting more and more attention because of its seriously potential environmental impact. Humic substances (HS), which lead to the difficulty of landfill leachate treatment, can also be recovered and used as a fertilizer for soil or remediation agent for contaminated sites. A 2500 Da ultrafiltration membrane was applied to separation of humic substances from salts and heavy metals in landfill leachate in this study. Humic substances recovery ratio was 50-70%. The fractional recovery of HS decreased from up to 100% to about 55% as concentration factor (CF) increased from 2 to 6. Fractional removals of  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  were up to 85%, 85%, 89%, and 51%, respectively. Fractional removals of heavy metals were more than 75%, 60%, and 78%, respectively. The 2500 Da UF performed well in separating HS from salts and heavy metals and in concentrating HS.

*Keywords:* landfill leachate, humic substances, ultrafiltration, 2500 Da, separation.

## 1 Introduction

Landfill leachate management is getting more and more attention because of its serious pollution to the environment and the treatment difficulties. Landfill leachate always contains a lot of refractory humic substances (HS), which may be simply classified into humic acid (HA) and fulvic acid (FA), and the HS content increases with landfill age [1–3]. The existence of HS affects significantly negatively the efficiency of biological treatment [4, 5], which is the predominant treatment process of landfill leachate all over the world. In recent years, advanced biological techniques such as the Membrane Bio-reactor (MBR)



technique have been widely adopted to treat landfill leachate, but the effluent cannot meet the discharge control criteria. Consequently, the bio-treated leachate usually requires further treatment with nanofiltration (NF) or reverse osmosis (RO) to meet the stringent effluent discharge criteria. This results in very expensive operation costs while generating plenty of retentates which are more refractory due to the enriched HS [6–8].

HS are naturally occurring mixtures of organic compounds that play an important role in both pollutant chemistry and biogeochemistry of natural waters and soils [9]. The chemical composition, structure, and characteristics of HS from landfill solid and leachate have been investigated by many researchers [10–12]. Chemical features of HS provide the potential to utilize HS as an agent for fertilization [2] and/or pollution remediation [13]. Separation of HS from landfill leachate can not only recover bio-fertilizer from waste, but also reduce the cost of landfill leachate treatment. Previous research has been conducted to separate and recover HS from leachate via an ultrafiltration (UF) device (1000 Da) [2]. In this paper, the efficiency of 2500 Da UF membrane for separating HS from landfill leachate was investigated.

## 2 Materials and methods

### 2.1 UF device for HS recovery

The HS separation process is shown in Figure 1. Spiral-wound membrane components (MWCO 2500 Da), purchased from General Electric Co. (Detroit, MI), were used in the system. Landfill leachate stored in the stock solution reservoir first flows through the security filter to remove large materials, and

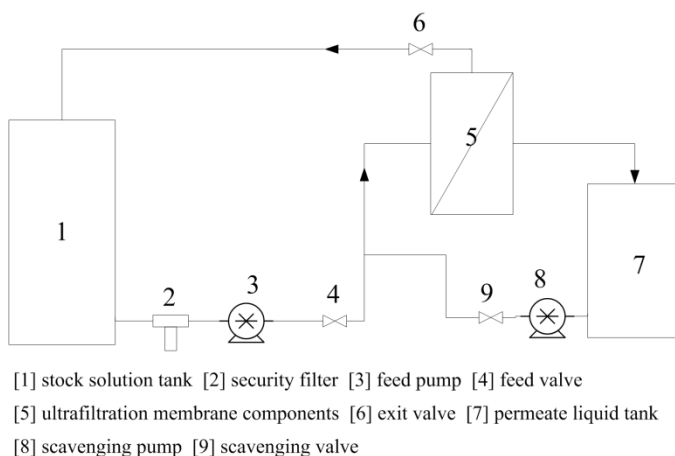


Figure 1: UF equipment for separating HS from landfill leachate.

then is pumped into the UF membrane module. After that, the permeate liquid is piped into permeate liquid tank, and the retentate is pumped back to the stock solution reservoir. The equipment was operated continuously until the expected concentration factor (CF), which was defined as the ratio of influent volume to concentrate volume, was achieved.

## 2.2 Analytical methods

The extraction and preparation method of HS was referred to the procedure employed by Christensen et al. [14]. Firstly, hydrochloric acid was added to the leachate samples until reaching a pH value of 1.0, and then the samples were placed overnight. Secondly, the precipitate in the samples was separated by centrifugation at 4000rpm for 20 minutes. This precipitate corresponded to HA. The concentration of HA was calculated as the difference of DOC between the stock solution and the supernate. Thirdly, having been adjusted to a pH value 2.0 with 5.0M NaOH, the supernate was pumped onto a Chromatography Column with Amberlite XAD-8, which can adsorb FA after prior acidification of samples. After that, FA was desorbed with 0.1M NaOH washing. Salts and heavy metals were analyzed by ICP-AES (Thermo Electron Co.).

## 3 Results and discussion

### 3.1 Concentration of HS

Figure 2 shows the variation of HS purity with separation pressure and CF. The purity of HS in concentration solution varies little with CF. When the pressure was between 0.7 MPa and 1.1 MPa, the purity of HS was about 10% higher than the feed (40%), while it was about 30% higher under 1.2 MPa, probably resulting from the ease at which low molecular weight organics can pass through UF membrane with a high pressure.

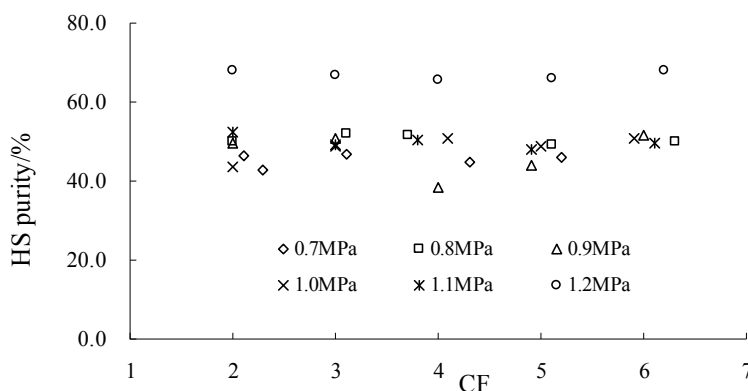


Figure 2: Variation of HS purity.



It is believed that HS has various molecular weights. Smaller ones enter the permeate driven by the pressure. Figure 3 shows the fractional recovery of HS with pressure and CF. With the lower CF (2–4), the fractional recovery of HS under low pressure was higher than that under high pressure, and the trend was reverse under the higher CF (4–6). When CF increased from 2 to 6, the fractional recovery of HS decreased from up to 100% to about 55%. The change of fractional recovery of HS varied with pressure. Under 0.7 MPa–0.9 MPa, the droop rate of the fractional recovery of HS increased as the pressure increased, while under 1.0–1.1 MPa, the droop rate of the fractional recovery of HS decreased.

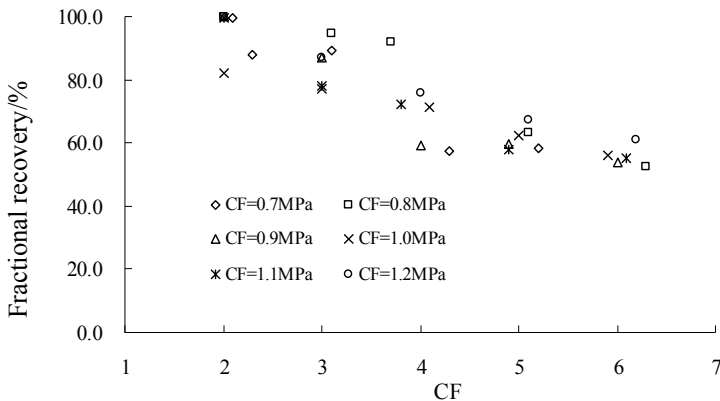


Figure 3: Fractional recovery of HS.

3.2 Removal of inorganic salts

Figures 4 and 5 show the fractional removal of  $K^+$  and  $Na^+$  under different pressure. The UF used in experiment could remove  $K^+$  and  $Na^+$  effectively. With

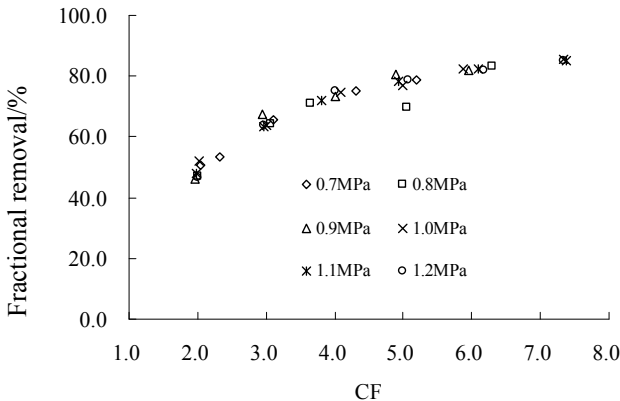
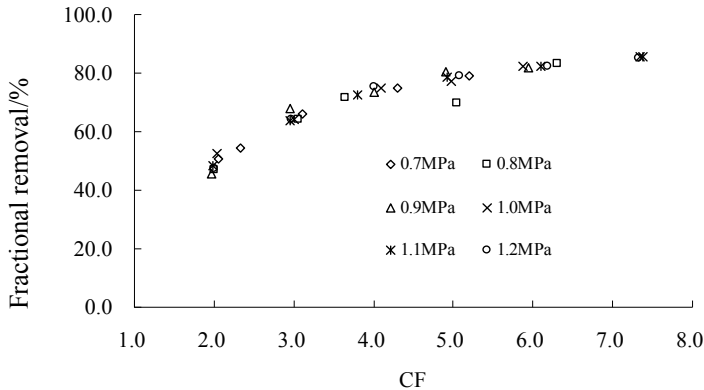


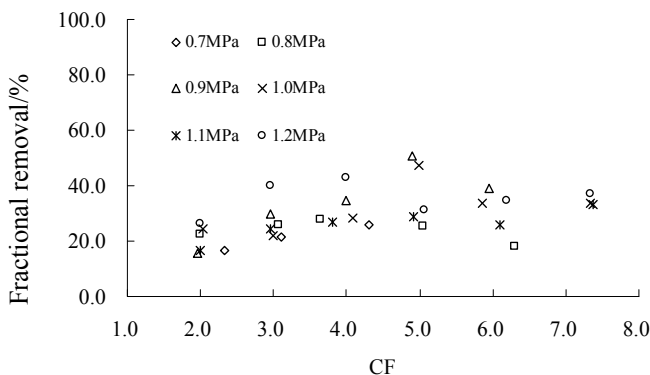
Figure 4: Fractional removal of  $K^+$ .



Figure 5: Fractional removal of  $\text{Na}^+$ .

the increase of CF, the fractional removal could be divided into two stages. When CF was between 2 and 4, the fractional removals of  $\text{K}^+$  and  $\text{Na}^+$  increased dramatically from 45% to 75%, while CF was bigger than 5, they increased slowly from 78% to 85%.

Figures 6 and 7 show the fractional removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with pressure and CF. The fractional removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were lower than that of  $\text{K}^+$  and  $\text{Na}^+$ . With the increase of CF, the fractional removal increased from 16% to 37%–51% for  $\text{Ca}^{2+}$ , from 44% to 83%–89% ( $\text{CF} \geq 5$ ) for  $\text{Mg}^{2+}$ . The distinguished difference between the fractional removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was because of the huge amount of carbonate (2000mg/L–3000mg/L) combine with  $\text{Ca}^{2+}$  into precipitated  $\text{CaCO}_3$  under the basic circumstance ( $\text{pH}=8$ ), thereby decreasing the fractional removal of  $\text{Ca}^{2+}$ .

Figure 6: Fractional removal of  $\text{Ca}^{2+}$ .

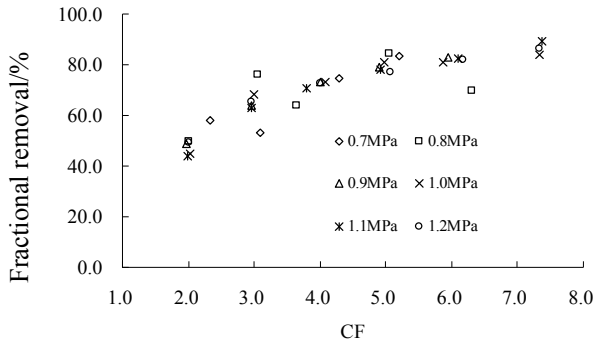


Figure 7: Fractional removal of  $Mg^{2+}$ .

Figure 8 shows the fractional removal of  $Fe^{2+}$  with pressure and CF. Different from the inorganic salts mentioned above, the fractional removal of  $Fe^{2+}$  was 5.8% to 14.5%. It was possible that the  $Fe^{2+}$  combined with some of the organic matter in the leachate and was being intercepted in the concentrate mostly.

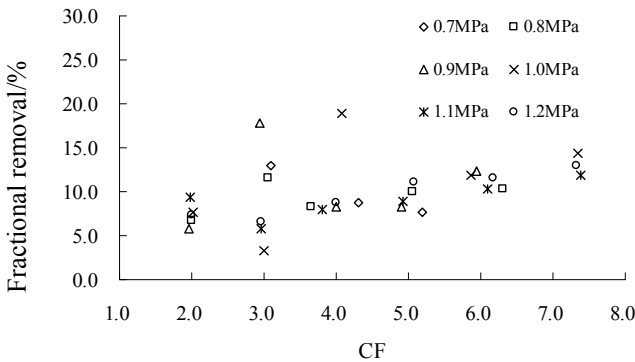


Figure 8: Fractional removal of  $Fe^{2+}$ .

The 2500 Da UF performed well in removing  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$  with CF between 5 and 7. The lower fractional removal of Ca might be because of the precipitation of  $CaCO_3$ . The operation pressure had little impact on the removal of inorganic salt ions. The  $Fe^{2+}$  combined with some of the organic matter in the leachate and was intercepted in the concentrate.

### 3.3 Removal of heavy metals

In the leachate there were heavy metals such like Zn, Ba, Mn, Cu, Cr, Pb, As and Ni, whose concentrations are shown in table 1. The removal of heavy metal by UF was investigated.



Table 1: Concentrations of heavy metals in leachate (mg/L).

Item	Value	Item	Value
Zn	1.00	Pb	0.23
Ba	1.21	As	4.08
Mn	0.52	Ni	0.10
Cu	0.16	Cr	0.17

Results showed that Cu, Cr and Ni cannot be removed from the leachate because they have strong ability to coordinate with HS. Figures 9 and 10 are the fractional removal of Ba and Mn with pressure and CF. Pressure did not impact the fractional removal very much. Their fractional removals increased with the

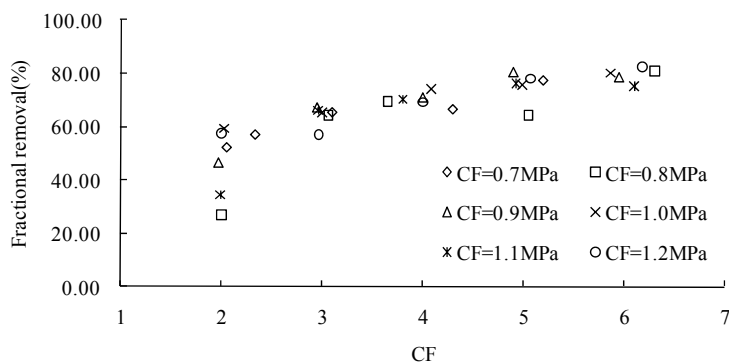


Figure 9: Fractional removal of Ba.

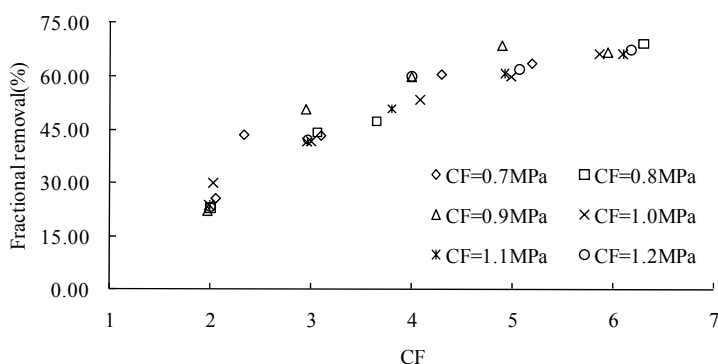


Figure 10: Fractional removal of Mn.



CF. When CF was larger than 5, the fractional removal of Ba and Mn were more than 75% and 60%, respectively. The UF can remove Ba and Mn well.

Figure 11 shows the fractional removal of As with pressure and CF. The fractional removal increased with the CF. The fractional removal was larger in high pressure (1.0, 1.1, 1.2 MPa) than that in low pressure (0.7, 0.8, 0.9 MPa). With the increasing CF, the gap between fractional removals under high and low pressure decreased. When CF was 5, the fractional removals were almost the same and more than 78%.

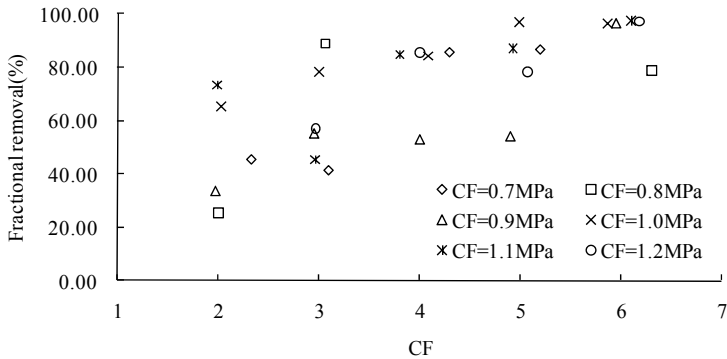


Figure 11: Fractional removal of As.

Figures 12 and 13 are the fractional removal of Zn and Pb with pressure and CF. Under all pressure conditions, the fractional removal of Zn increased with CF. Pb followed the similar rules with Zn expect that under 0.7 MPa the fractional removal of Pb decreased before it increased. Pressure did not impact fractional removal apparently. When CF was larger than 5, the fractional removal of Zn was higher than 50%, while that of Pb was higher than 60%.

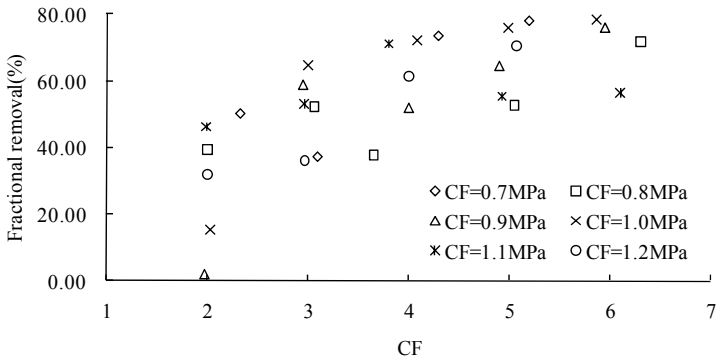


Figure 12: Fractional removal of Zn.





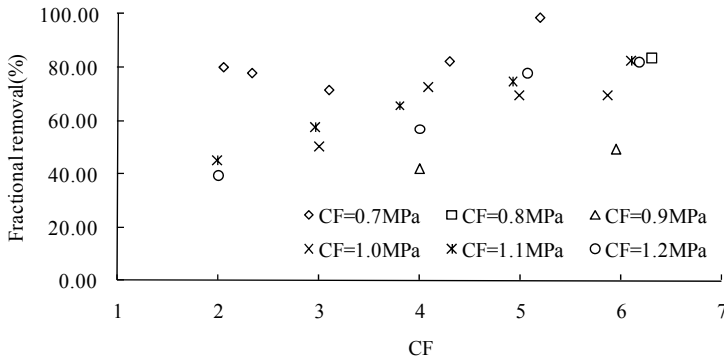


Figure 13: Fractional removal of Pb.

## 4 Conclusions

A 2500 Da UF was applied to separate HS from salts and heavy metals in landfill leachate. The purity of HS was about 50% when the pressure was between 0.7 MPa and 1.1 MPa and about 70% when the pressure was 1.2 MPa. The fractional recovery of HS decreased from up to 100% to about 55% as CF increased from 2 to 6. Fractional removals of  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  were up to 85%, 85%, 89%, and 51%, respectively. Fractional removals of heavy metals were more than 75%, 60%, and 78%, respectively. The 2500 Da UF performed well in separating HS from salts and heavy metals and in concentrating HS.

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