MEMBRANE SEPARATION PROCESSES IN PRACTICE – LANDFILL LEACHATE TREATMENT

Marek Šír[1)], **Zuzana Honzajková**[1)], **Pavla Hrychová**[1)], **Martin Bystrianský**[1)], **Radek Vurm**[1)], **Pavel Kocurek**[2)]

[1)]*University of Chemistry and Technology Prague, Department of Environmental Chemistry, Technická 5, Prague 6,166 28, Czech Republic, e-mail: sirm@vscht.cz*

[2)]*Tomas Bata University in Zlín, Faculty of Applied Informatics, Nad Stráněmi 4511, 76005, Zlín, Czech Republic*

Abstract

This paper deals with the membrane fouling by humic acids contained in landfill leachate and it represents a part of a comprehensive solution for the removal of landfill leachate using membrane separation processes. Humic acid content in the leachate changes depending mainly on the age of the landfill. Separation experiments were performed with raw leachate and with leachate adjusted by the addition of 20 mg/L, 40 mg/L and 50 mg/L of humic acids. In the case of raw leachate treatment, concentration of inorganic salts decreased from 7200 mg/L to 50 mg/L in the permeate. The concentration of organic substances, expressed as total organic carbon (TOC), was reduced from 225.6 mg/L in the leachate to 6.2 mg/L in the permeate. Natural content of humic acids in raw leachate was 18 mg/L. After the addition of 50 mg/L of humic acids, permeation flux decreased by 18% on average and the separation efficiency decreased by 20% on average.

Key words:

membrane separation processes, reverse osmosis, nanofiltration, membrane fouling, landfill leachate

Introduction

Membrane separation processes are used in many industries associated with the production (drinking and industrial water) or disposal (industrial waste water) liquid solutions. These processes are also used for treatment of complicated water in terms of composition, such as e.g. landfill leachate. Many studies confirming the high removal efficiency of undesired components from the treated solution (Peters, 1998; Rena et al., 2008). In some cases, however, a combination with other technologies and the proper pre-treatment of the input stream to remove the negative effects on the membrane is required. Negative effects are e.g the formation of deposit on the membrane surface (Mikulášek et al., 2013). One of the groups of substances which are involved in the formation of deposits on the membrane surface are humic acids (HA) (Ang et al., 2006; Tang et al., 2007; Šír, et al., 2012; Martel-Meliana N. et al ., 2012).

Organic matter contained in landfill leachate is composed mainly of fatty acids with short and long-chain and humic substances. The weighting is due to the age of the landfill. Young landfills contain mainly fatty acids (Harmsen. 1983), while in older landfills consists organic matter predominantly humic substances (humic acids, fulvic acids and humins) up to 60% (Artiola-Fortuna, Fuller, 1982). The concentration of humic substances in landfill leachate can reach from tens of mg/L (Christensen et al., 1998; Gron, et al., 1996) to hundreds of mg/L (Bertha, et al., 2008; Liang et al., 2009) depending on the type of waste being deposited and on the age of the landfill.

This paper deals with the problem of membrane fouling by humic acids contained in landfill leachate and form part of a comprehensive solution for the removal of landfill leachate using membrane separation processes.

Materials and methods

Membrane separation unit LAB M240 was used for the experiments. The equipment consists of a storage tank with a capacity of 50 liters membrane pump Wanner G10XK 1LA7 equipped with Siemens motor with a frequency converter and the membrane module. Pump is able to pump the acidic and basic solutions with solids contents up to 1 mm. Membrane module is a plate DT LabStak® M20 module manufacturer by Alfa Laval and allows the use of any flat membrane. In all experiments, reverse osmosis (RO) membranes RO98pHt were used (Alfa Laval). It is a composite membrane with a thin separating layer consisting of a polyamide, and which is supported by polypropylene. The active area of each membrane is 0.0174 m^2. Membrane can operate in a wide pH range (2-11) and pressure up to 6 MPa. The required working pressure is set by regulation of the main pressure valve, which is located at the output of membrane module. The flow rate of the treated water is provided by a pump. Flow rate can be selected in the range of 5 - 15 L/min. Temperature control is done by adjusting the flow of cooling water through heat exchangers. The value of working pressure can be read from two analog gauges located upstream and downstream of the membrane module. Differential pressure on both gauges allows you to check the current pressure drop across the membrane module. The equipment is designed to work in batch mode.

Separation experiments with raw landfill leachate were carried out in a single-stage batch arrangement. The input volume was 15 L, the concentration factor achieved was c_f = 10, operating pressure was 3 Mpa and operating temperature 20 °C. During the process the flow of permeate, conductivity of input stream, permeate and concentrate were measured continuously. After the process cleaning procedure has been applied by adding an alkaline cleaning using detergent (Ultrasil, Henkel) at pH 10 and the acidic cleaning by the addition of HCl at pH 2. The effectiveness of the cleaning procedure was verified by measuring of permeation performance under the constant conditions (p = 2 MPa and t = 20 °C).

Subsequently, stock solution of humic acid concentration of 8 g/L was prepared. This solution was then used to prepare working solutions of three landfill leachate with concentration of added humic acids 20 mg/L, 40 mg/L and 50 mg/L. Working solutions were treated using RO similarly as raw leachate.

To determine the parameters of the separation processes the following relationships were used: the selectivity of the membrane against the separated mixture is expressed by the rejection (retention):

$$R = \frac{c_s^f - c_s^p}{c_s^f} \tag{1}$$

where c_s^f is the concentration of component in input stream
c_s^p is the concentration of component in permeate

Rejection is usually expressed as a percentage. To determine the rejection for continuous measurement during a separation experiment, conductivity of input stream and the conductivity of the permeate used were used instead of the concentration of separated components.

Rate of concentration of the separated solution in the batch process is given by the concentration factor:

$$c_f = \frac{V_{F0}}{V_C} \tag{2}$$

where V_{F0} is the total input volume
V_c is the volume of concentrate

Following methods were used for analytical analysis: Metals were determined by atomic absorption spectrometry / atomic emission spectrometry analyzer SensAA (GBC Scientific Equipment), anions were determined by capillary zone electrophoresis CAPEL - 105M (Lumex), liquiTOC II analyzer (Elementar Analysensysteme GmbH) was used for the determination of total organic and inorganic carbon, pH was measured using a digital pH meter GMH 3530 (Greisinger Electronic) and conductivity was measured by a digital conductivity meter GMH 3430 (Greisinger Electronic).

The concentration of humic acid was measured by a modified spectrophotometric method (Sheng et al., 2007) based on the complex formation by the reaction of humic acid with toluidine blue. The absorbance of the resulting solution was measured at a wavelength of 603 nm in a 5 cm cuvette using a spectrophotometer UV / VIS Cintra 101 (GBC Scientific Equipment).

Results and discussion

Results of the analysis of the individual technological streams are summarized in Tab. 1. It shows the analysis of the landfill leachate, permeate and concentrate and rejection of individual components. Natural content of humic acids in leachate was c(HA) = 18 mg/L

Table 1: Analysis of the individual technological streams and treatment efficiency.

Parameter	Unit	Input	Permeate	Rejection (%)	Concentrate
SO_4^{2-}	mg/L	1970	10	99,5	15900
Cl^-	mg/L	1850	50	97.3	16600
NO_3^-	mg/L	0.83	0.04	95.2	33.2
F^-	mg/L	2.75	0.1	96.4	12
Ca	mg/L	433	1.0	99.8	2 660
Mg	mg/L	217	5.0	97.7	1 880
Na	mg/L	1530	12.3	99.2	14710
K	mg/L	330	4.3	98.7	3990
Fe	mg/L	0.33	0.0037	98.9	3.58
Mn	mg/L	1.67	0.0064	99.6	4.50
Cr	mg/L	0.031	<0.0005	>98.4	0.29
As	mg/L	0.94	0.027	97.1	8.60
N_{ammon}	mg/L	142	8.54	94.0	1110
HCO_3^-	mg/L	506	13.7	97.3	2420
TOC	mg/L	226	6.15	97.3	2010
BTEX	μg/L	130	2.0	98.5	13
TDS	mg/L	7200	50	99.3	53300
Rejection	μS/cm	11600	165	98.6	65200
pH	-	7.7	6.2	-	7.5

High removal efficiency of the individual components is determined by the type of membranes used and it is consistent with previous studies (Peters, 1998; Rena et al., 2008). Problematic component of leachate proved to be ammonia nitrogen, which was removed from only 94% under the conditions. The concentration of this component is in terms of discharge into surface water quite limited. Therefore, if the limits are not met, concentration of ammonia nitrogen in the permeate can be reduce by the number of ways: application of the second stage RO, acidification of the input stream and sliding equilibrium with ammonia in favor of better separated ammonium ion NH^{4+}, sorption on natural substances like zeolite and clinoptilolite, or by precipitation as struvite ($MgNH_4PO_4$. 6 H_2O).

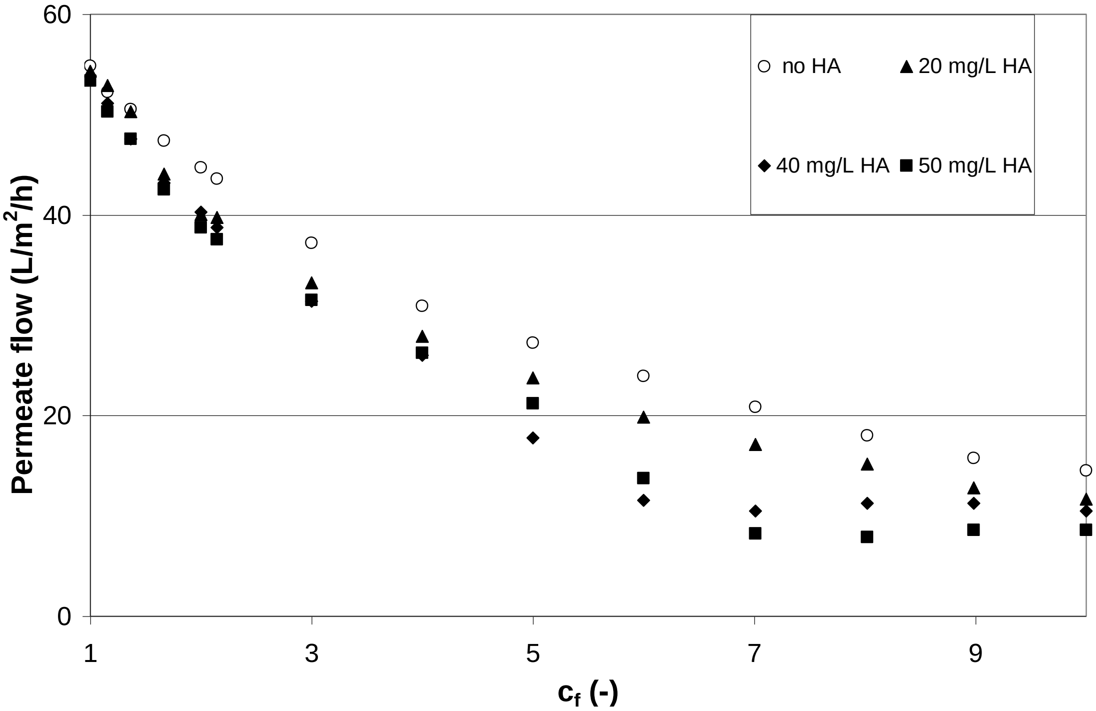

Fig. 1: Effect of added humic acids (HA) concentration on flux performance of membrane in batch mode.

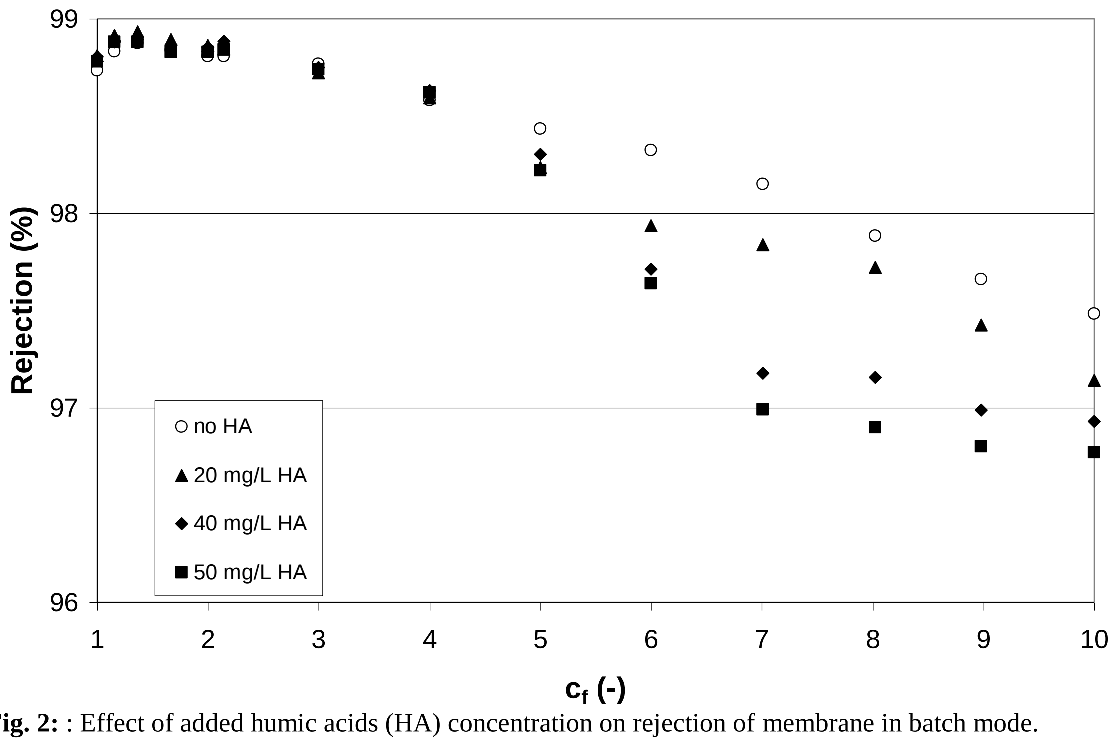

Fig. 2: : Effect of added humic acids (HA) concentration on rejection of membrane in batch mode.

In the studied range (c (HA) = 0 - 50 mg/L) addition of humic acids caused significant reduction in permeation flux (Fig. 1), and decreased average efficiency of removal of leachate components while achieving concentration factor $c_f \geq 5$ (Fig. 2). When adding 50 mg/L of humic acid permeate flow decreased by an average of 18% and rejection of components decreased by an average of 20%. These phenomena can be explained by the creation of a secondary semi-permeable layer on the membrane surface. Consequently deteriorated hydrodynamic parameters in this layer leads to increasing of the concentration of the components near the membrane surface and thereby to increase the concentration of these components in the permeate.

In terms of membrane fouling the issue of treatment of landfill leachate is more complicated. During the process of concentrating the treated solution the solubility of some components can be exceed and thus their crystallization can be started. In this case the crystallization either in bulk solution (initiated by homogeneous nucleation or heterogeneous nucleation of solution components), or the crystallization on the surface of the device and the membrane (due to heterogeneous nucleation) may occur. The second variant causes blockage of membrane surface and very rapid decline of permeation performance. The solution may be antiscalant dosage or insert crystallization step after the separation process. Interposing recrystallization of concentrate can contribute to the removal of part of the salts, reducing the osmotic pressure of the solution and achieve a higher overall concentration factor (Rautenbach, Linn, 1996; Wu, 2011). The purified water can be used directly on reclaimed parts of the landfill or discharged into receiving waters. Also, a certain proportion of landfill leachate (humidity) in the landfill body is desirable in terms of generating of landfill gas. The proposed scheme of removal and recirculation of landfill water is shown in the following picture (Fig. 3).

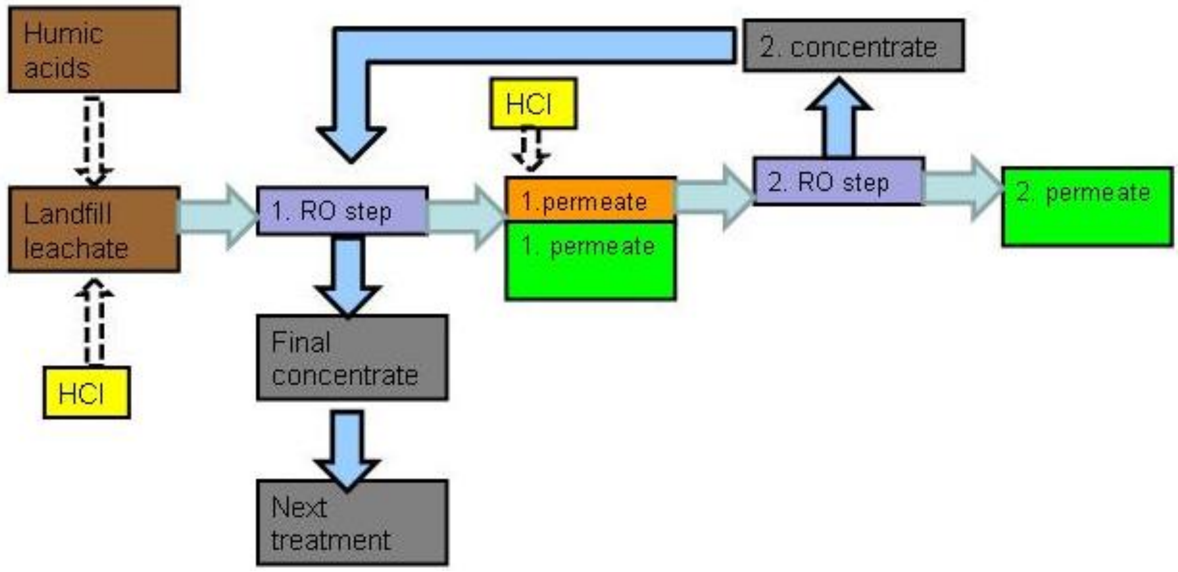

Fig. 3: The overall scheme of leachate processing using a membrane separation process.

Conclusion

This study dealt with membrane fouling experiments studying the influence of humic acids on the permeate flow and total rejection of leachate components. Content of humic acids increse with the age of the landfill.

Main conclusions is that the separation process decreased the concentration of inorganic salts from 7200 mg/L in the leachate to 50 mg/L in the permeate. The concentration of organic substances, expressed as TOC, was reduced from 225.6 mg/L in the leachate to 6.2 mg/L in the permeate. Membrane fouling experiments showed, that the permeate flux and the rejection decreased with the increasing concentration of added humic acids. The decrease also depended on the achieved concentration factor in batch mode. The decrease was 18% on average for the permeate flux and 20 % on average for the rejection, when 50 mg/L humic acids were added and the concentration factor cF = 10 was reached. Leaching of wastes containing humic acids may adversely affect the separation efficiency of the other leachate components. This paper is part of the complex solution for landfill leachate treatment including several process steps.

Acknowledgement

Financially supported by MSM6046137308.

Literature

Ang W.S., Lee S.Y., Elimelech M. 2006. Chemical and physical aspect of cleaning of organic-fouled reverse osmosis membranes, J. Membr. Sci. 272, pp. 198–210.

Artiola-Fortuny J., Fuller W.H. 1982. Humic substances in landfill leachates: I. Humic acid extraction and identification, J. Environ. Qual. 11, pp. 663–668.

Berthe C., Redon E., Feuillade G. 2008. Fractionation of the organic matter contained in leachate resulting from two modes of landfilling: an indicator of waste degradation, J. Hazard. Mater. 154, pp. 262–271.

Christensen J.B., Jensen D.L., Gron C., Filip Z., Christensen T.H. 1998. Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater, Water Res. 32, pp. 125–135.

Gron C., Wassenaar L., Krogh M. 1996. Origin and structures of groundwa-ter humic substances from three Danish aquifers, Environ. Int. 22, pp. 519–534.

Harmsen J. 1983. Identification of organic compounds in leachate from a waste tip, Water Res. 17, pp. 699–705.

Liang Z., Liu J.X., Li J. 2009. Decomposition and mineralization of aquatic humic substances (AHS) in treating landfill leachate using the Anammox process, Chemosphere 74, pp. 1315–1320.

Melián-Martel N. et al. 2012. Structural and chemical characterization of long-term reverse osmosis membrane fouling in a full scale desalination plant. Desalination 305, pp. 44-53.

Mikulášek P. et al. 2013. Tlakové membránové procesy. Praha: Vysoká škola chemicko-technologická v Praze, ISBN 978-80-7080-862-7.

Peters T.A. 1998. Purification of landfill leachate with reverse osmosis and nanofiltration, Desalination 119, pp. 289–295.

Rautenbach R., Linn T. 1996. High-pressure reverse osmosis and nanofiltration, a “zero discharge” process combination for the treatment of waste water with severe fouling/scaling potential, Desalination 105, pp. 63–70.

Renou S., Givaudan J.G., Poulain S., Dirassouyan F., Moulin P. 2008. Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150, pp. 468 -493.

Sheng G.P., Zhang M.L., Yu H.Q. 2007. A rapid quantitative method for humic substances determination in natural waters, Anal. Chim. Acta 592, pp. 162–167.

Šír M., Podhola M., Patočka T., Honzajková Z., Kocurek P., Kubal M., Kuraš M. 2012. The effect of humic acids on the reverse osmosis treatment of hazardous landfill leachate, J. Hazard. Mater., 207-208, pp. 86-90.

Tang C.Y, Kwon Y.N., Leckie J.O. 2007. Fouling of reverse osmosis and nanofiltration membranes by humic acid – effects of solution composition and hydrodynamic condition, J. Membr. Sci. 290, pp. 86–94.

Wu Y., Zhou S., Chen D., Zhao R., Li H. and Lin Y. 2011. Transformation of metals speciation in a combined landfill leachate treatment. Science of the Total Environment 409, pp. 1613-1620.