

The effect of humic acids on the reverse osmosis treatment of hazardous landfill leachate

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ABSTRACT

This study deals with the treatment of hazardous waste landfill leachate with the help of reverse osmosis. The landfill is located in an abandoned brown coal pit in northern Bohemia. The leachate contained 7.2 g/L of dissolved inorganic salts. Among other contaminants were heavy metals, arsenic, ammonia nitrogen and associated organic pollutants, especially chlorinated compounds. A mobile membrane unit (LAB M30) equipped with a spiral wound element (FILMTEC SW30-4040), with a membrane area equaling 7.4 m² was used for the pilot plant experiments. All experiments were carried out in batch mode. 94% conversion of the input stream into the permeate was achieved by use of a two-stage arrangement. Removal efficiencies of the monitored contaminants in the feed ranged from 94% for ammonia nitrogen to 99% for the two-valent ions. Removal efficiency for total dissolved solids was 99.3% on average.

Due to varying levels of humic acids in the leachate throughout the year, fouling experiments were performed to investigate the separation process under different conditions than those used in the pilot plant. Leachates containing different concentrations of added humic acids were separated using a thin film composite on a propylene membrane. The added humic acids were obtained from samples of contaminated oxihumolite.

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1. Introduction

1.1. Application of reverse osmosis for landfill leachate treatment

Treatments based on membrane technology, like biodegradation and chemical and physical methods (chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation or air stripping), are viable alternatives to conventional methods of landfill leachate treatment. All pressure-driven membrane separation processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) are used in the treatment of landfill leachate. Reverse osmosis appears to be the method of choice for the purification of landfill leachate, because it separates on an ionic level. Besides removing organic contaminants, reverse osmosis also removes dissolved inorganic salts. Values of the rejection coefficient higher than 99% were reported [1].

One of the first operational applications of reverse osmosis was installed in the wastewater treatment plant in the town of Wijster in the Netherlands in 1986. The two-stage unit employed tubular membrane modules in the first stage and spiral-wound membrane modules in the second stage with total recovery rate of 54%. The

permeate from the second stage meets required limits for discharge into natural water streams [2]. Significant advancement in this field occurred with the development of the desk tubular modules, in which flat membranes are placed between desks in a tube. In the last decade, more than one hundred technological systems using reverse osmosis were installed at landfill sites in Northern Europe, North America and the Far East [3]. An example is one of the largest facilities in Europe, a two stage reverse osmosis installation at a landfill in Ihlenberg, Germany. The DT modules in the first stage have a total area of 1147 m², the second stage uses spiral wound modules totaling an area of 768 m². Separation efficiencies of organic and inorganic substances fall within the 98–99% range [4]. Reverse osmosis is also used in combination with other technologies, most often with biological pre-treatment, as is the case for landfills in Mechernich and Kolenfeld, Germany [5]. A two-stage reverse osmosis system with a capacity of 500 m³/day and recovery rate of 80% was put into operation in October 2003 at the Changshengqiao landfill in the city of Chongqing, China. The pH of the leachate was adjusted from 6.0 to 6.5 to prevent premature precipitation. After filtration, the leachate was fed into the first stage of reverse osmosis. The second stage permeate was discharged into the river and the second stage concentrate was recycled into the first stage. The concentrate resulting from that first stage was returned to the landfill body. The separation efficiency for most of the components was 99% and removal of certain ions such as Ca²⁺,

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Ba²⁺, and Mg²⁺ was accomplished with an even greater efficiency of 99.9% [6]. Recovery rates depend on operating pressure, conditions of separation and the composition of leachate. Recovery rates higher than 95% were reported when high-pressure RO units were used at the Ihlenberg landfill in Germany [7].

In the Czech Republic, membrane separation processes are used in many industrial sectors (food, pharmaceuticals, etc.). However, for the treatment of leachate they have mainly been used in pilot plant tests at limited locations. Among the examples of successful application is the decontamination of a landfill in eastern Bohemia (Nový Rychnov). Groundwater here was contaminated by chlorinated hydrocarbons, organochlorine pesticides, nitrites, chlorides, heavy metals and other substances. Reverse osmosis was used here as a final purification technology after stripping and filtration with activated carbon. Another example includes the pilot plant tests performed at a disposal site for fly-ash and desulfurization products from a power generating plant in Prunéřov. The effectiveness of commercial antiscalant to mitigate scaling of calcium sulfate was tested. A membrane unit with the capacity of 5 m³/day and a recovery rate of 80% was used. The average separation efficiency was 99%.

Fouling of reverse osmosis membranes causes significant losses to productivity and adds to operational costs. Organic matter, such as humic acids, have been identified as one of the major foulants for membranes [8]. Humic acids comprise a group of heterogeneous polymeric organics. Their molecular weights range from a few thousand to a few hundred thousand Daltons, depending on their source [9].

Organic matter contained in municipal landfill leachates includes mainly volatile fatty acids and humic substances. Content of the two organic fractions in leachate varies greatly depending on the landfill age. In young landfills, a majority of organic carbon is present as volatile fatty acids [10]. However, in mature landfills, humic substances (humic acids, fulvic acids, and humins) dominate the organic fraction in methanogenic leachate by as much as 60% [11]. Concentrations of humic acids in the range of units to tens mg/L in landfill leachates were reported in previous studies [12–14]. The content of humic acids is also greatly dependent on the type of deposited waste and the type of landfill, so concentration in hundreds mg/L are presented in some studies [15,16].

There are a limited number of systematic studies on the fouling of reverse osmosis membranes by humic acids [17]. However, most previous studies focused on fouling during the separation of model solutions. The objective of this study is to investigate the effects of humic acids on the separation of a complex solution, which is represented by the hazardous landfill leachate.

1.2. Investigated locality

The investigated landfill is located in northern Bohemia and is used for waste management of both hazardous and non-hazardous wastes. The landfill has been in operation since 1993. It consists of two disposal sites located in an abandoned open-cast brown coal mine. The landfill has a total capacity of 1.7 million m³. According to a hydro-geological survey, the natural circulation of water around the landfill has been significantly disrupted. The leachate flows through a drainage system into a central shaft, then pumped into concrete cofferdams located outside the landfill body, and subsequently fed to the city wastewater treatment plant. The daily production of leachate averages 80 m³. The leachate contains large quantities of total dissolved solids (about 7 g/L). Other contaminants include heavy metals, arsenic and associated organic pollution. The leachate composition varies minimally during the year, primarily depending on rainfall. Upon its closure, the landfill will be insulated with the aid of sealing elements so as to

prevent infiltration of rainwater into the landfill body, and the surrounding area will be rehabilitated and reclaimed. Given the high percentages of inorganic salts and biologically recalcitrant organic compounds, the leachate cannot be purified in a municipal wastewater treatment plant. Therefore, the site managers are considering the introduction of reverse osmosis technology that would remove most of the contaminants. The purified stream, depending on its quality, would be either drained into the public sewer system or discharged directly into a water recipient.

The possibility of temporary deposition of approximately 30 000 tons of contaminated oxihumolite (is young weathered lignite with low calorific value and high sorption capacity) on the bioremediation site next to the landfill appeared after the pilot plant experiments. Leachate from this site is drained into the same shaft as the landfill leachate, thus affecting its composition. In the past, 23 000 tons of contaminated oxihumolite from nearby highway construction was stored there. This procedure temporarily increased the content of humic acids in landfill leachate by almost three times (from 14 mg/L to 40 mg/L). The original content of humic acids in the leachate is partly caused by leakage of the landfill body, which is infiltrated by ground water from an abandoned open-cast brown coal mine and it ranging between 11 and 20 mg/L in the last 5 years.

2. Materials and methods

2.1. Pilot plant experiments

A series of laboratory tests to investigate the effects of various pretreatment methods on the separation process and the quality of the permeate preceded the reverse osmosis pilot plant tests. Pretreatment included filtration, pH adjustment to acidic by addition of HCl, alkaline precipitation with NaOH and CaO, as well as filtration with activated carbon.

Based on the laboratory results, a reverse osmosis unit consisting of two consecutive stages, in which the concentrate leaving the first stage becomes the input stream to the second stage, was selected for pilot plant testing. This arrangement satisfied the requirement for minimizing the volume of the final concentrate. The only pretreatment used in the pilot plant tests was the filtration of crude leachate through a cloth filter. One supplementary experiment was conducted in which the feed to the first reverse osmosis stage was acidified to pH 5 with the help of hydrochloric acid. Experiments were carried out in batch mode. Input volume of the leachate to the first reverse osmosis stage was 200 L for each experiment. A total of five experiments were carried out separating the leachate in the first reverse osmosis stage in order to produce sufficient amount of the concentrate, which was then stored in a special container. The concentration factor (c_F) of the first RO stage was $c_F = 10$. Concentration factor is expressed by the following definition: $c_F = V_i/V_c$, where V_i is input volume and V_c is the volume of remaining concentrate. 50 L of stored concentrate were used as the input in the second reverse osmosis stage. The concentration factor of the second RO stage was $c_F = 1.67$. Regarding to the anticipated operational pressure in a full scale reverse osmosis plant, all experiments were performed at an applied pressure of 3 MPa. The operating temperature was set to 20 °C, and maintained by a heat exchanger. The rejection rate was chosen in regard to the permeate output, which was measured continuously throughout the experiment.

After each experiment, membranes were flushed with tap water and both acidic and alkaline cleaning was performed in order to remove possible carbonate and organic sediments. First, dilute hydrochloric acid was added to the flush water to acidify it to pH 2. After rinsing of the acid, alkaline detergent Ultrasil was dosed

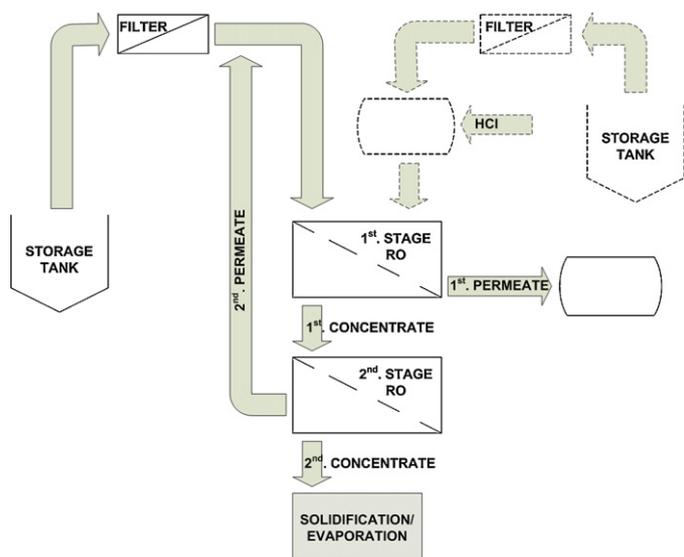


Fig. 1. Scheme of the technological steps for pilot plant experiments. The solid line shows the basic two-stage arrangement of reverse osmosis (RO); the dashed line shows the supplemental experiment with the acidified leachate.

until achieving pH 11.5. Then the device was again rinsed with tap water. Effective cleaning was confirmed by the measurement of permeate flux produced by reverse osmosis of tap water under standard conditions of 2 MPa and 20 °C. Fig. 1 shows the scheme of the technological steps.

Membrane unit LAB M-30 is designed for the pilot plant testing of pressure driven membrane separation processes such as reverse osmosis and nanofiltration. The unit is equipped with a container for RO/NF elements of the standard “4040” size (i.e., diameter 4 in., length 40 in.). The module is equipped with an integrated Clean-in-Place (CIP) system and can be used to test the effectiveness of different methods of membrane cleaning.

Basic technical data: membrane element – FILMTEC SW30-4040, active membrane area – 7.4 m², standard permeate flux – 300 L/h, maximum operating pressure – 6.9 MPa.

2.2. Membrane fouling experiments

A series of experiments were performed to determine the effect of humic acids on the separation process. Humic acids were isolated with the help of the procedure described by Rowell [18] from samples of contaminated oxihumulite, which is expected to be dumped on the remediation site located next to the landfill. In principle, the humic acids were leached out of the oxihumulite samples by 0.1 M NaOH alkaline solution and precipitated by HCl solution.

A stock solution containing 8 g/L of humic acids (pH ~8) was prepared and stored at 4 °C in the dark. The stock solution was subsequently diluted by filtrated landfill leachate to obtain three different working solutions, whose concentrations of humic acids were 20 mg/L, 40 mg/L and 50 mg/L.

Separation experiments were carried out in batch mode in one stage. Input volume of the leachate was 15 L. The concentration factor achieved was $c_F = 10$. All experiments were performed at a pressure of 3 MPa. The operating temperature was set to 20 °C. The permeate flow and the rejection rates were measured throughout the experiments. After each experiment, the membranes were flushed with tap water and both alkaline and acidic cleaning were performed. First, the alkaline detergent Ultrasil (Henkel) was dosed until reaching pH 12 to remove humic acids and other organic deposits. Then the device was again rinsed with tap water, and diluted hydrochloric acid was added to the flush water to acidify

it to pH 2. The effectiveness of cleaning was confirmed by measurement of the permeate flux produced by reverse osmosis of tap water under standard conditions of 2 MPa and 20 °C. Experiments were repeated 3 times.

Membrane unit LAB M-20 was used for laboratory experiments. This unit is equipped with a plate and frame module and is designed for the testing of separations on a small scale. Basic technical data: membrane module – LabStack M20, membrane – RO98pHt, thin-film composite on polypropylene, active membrane area – 0.625 m², standard permeate flux – 30 L/h, maximum operating pressure – 6.0 MPa.

2.3. Analytical methods

Conductivity and pH values were measured using GMH 3430 and GMH 3530 devices, respectively (Greisinger Electronic). Samples of the leachate, permeates and concentrates were stored at 4 °C before analysis. Metals and arsenic were measured with the atomic absorption and emission spectrophotometer SensAA (GBC Scientific Equipment). N_{amonn} was measured by spectrophotometric method after conversion to indophenol dye by the spectrophotometer (UV/VIS Cintra 101, GBC Scientific Equipment) at 655 nm. TDS were determined by gravimetric method at the temperature 105 °C. Anions (SO_4^{2-} , Cl^- , NO_3^- , F^-) were measured with the capillary electrophoresis system Capel 105 M (Lumex Ltd). The TOC and HCO_3^- values of samples were measured with the TOC/TN analyzer liquiTOC II (Elementar Analysensysteme GmbH).

BTEX were measured with the gas chromatograph (GC) FOCUS GC equipped with capillary column TR-V1 and with mass detector (MS) DSQ II (Thermo Scientific). GC method programme was as follows: initial temperature 60 °C, hold 2 min, rate 30 °C/min, final temperature 250 °C, hold 2.5 min; split flow 1:10. MS method programme was: source temperature 200 °C, mass range 15–500.

2.4. Determination of humic acids

The concentration of humic acids were determined by the modified spectrophotometric method [19] based on the binding of a dye toluidine blue (TB) to humic acids molecules to produce a dye–humic acids complex. Measurement was carried out by spectrophotometer (UV/VIS Cintra 101, GBC Scientific Equipment) at 603 nm, using 5 cm-long glass cells. Calibration curve showed very good correlation coefficient (>0.99) in the measured range (0–50 mg/L). TB solution (1.5 mM) of 1.0 mL and sodium citrate–phosphate buffer (0.05 M, pH 7.0) of 2.5 mL were added into a 10-mL tube. After that, 0.5 mL of 0.05 M EDTA solution was added to the tube to remove the potentially interfering cations (e.g., Ca^{2+} , Mg^{2+} and Fe^{3+}). The solution was then mixed and 4 mL distilled water or samples were added and immediately mixed. Thereafter, the tube was placed at ambient temperature for 20 min before the absorbance measurement using distilled water as a reference.

3. Results and discussion

3.1. Pilot plant experiments

The results of the analysis of individual technological streams are summarized in Table 1. It shows the analysis of the filtrated leachate, the first stage permeate and the second stage permeate and concentrate.

The composition of the first stage permeate shows greater than 99% removal of total dissolved solids (TDS), and more than 97% removal of organic substances, expressed as total organic carbon (TOC). The first stage permeate conductivity was 165 μ S/cm. The only indicator that exceeded limits set by the contracting authority

Table 1

Analysis of the individual technological streams for the two stage reverse osmosis for pilot plant experiments performed with no added humic acid.

Parameter	Unit	Input	First stage permeate	Rejection in %	Second stage permeate	Second stage concentrate
SO ₄ ²⁻	mg/L	1970	10	99.5	28.0	15 900
Cl ⁻	mg/L	1850	50	97.3	224	16 600
NO ₃ ⁻	mg/L	0.83	0.04	95.2	1.11	33.2
F ⁻	mg/L	2.75	0.1	96.4	<0.10	12
Ca	mg/L	433	1.0	99.8	<1.0	2660
Mg	mg/L	217	5.0	97.7	<5.0	1880
Na	mg/L	1530	12.3	99.2	110	14 710
K	mg/L	330	4.3	98.7	35.8	3990
Fe	mg/L	0.33	0.0037	98.9	0.0019	3.58
Mn	mg/L	1.67	0.0064	99.6	0.0087	4.5
Cr	mg/L	0.031	<0.0005	>98.4	<0.0005	0.29
As	mg/L	0.94	0.027	97.1	0.022	8.6
N _{ammon}	mg/L	142	8.54	94.0	46.3	1110
HCO ₃ ⁻	mg/L	506	13.7	97.3	66.5	2420
TDS	mg/L	7200	50	99.3	480	53 300
TOC	mg/L	226	6.15	97.3	6.24	2010
BTEX	μg/L	130	2	98.5	<2	13
Humic acids	mg/L	18	<0.8	>95.5	<0.8	145
Conductivity	μS/cm	11 600	165	98.6	1150	65 200
pH	-	7.7	6.2	-	6.8	7.5

was content of ammonia nitrogen. It is necessary to study its possible subsequent removal. One possibility would be to acidify the first stage permeate and to treat it in the second stage of reverse osmosis.

The data also show that the permeate from the second stage can be recycled into the input stream, as it has better quality than the first stage permeate and does not negatively change the properties of the first stage permeate. The second stage concentrate can be processed by its solidification or with the help of evaporation.

The permeate flux's dependence on the concentration factor was monitored. No abrupt decrease in the permeate output (which would signify a rapid membrane fouling) was observed. The permeate flux declined steadily, largely due to an increase in the osmotic pressure of the solution and also due to membrane fouling by gradually formed deposits. Acid and alkaline cleaning of the deposits was applied after each test. The permeate flux after each treatment was at a constant level of 42 L/m²/h.

A supplementary experiment was conducted with a leachate that was acidified to pH 5 by the addition of HCl. The experiment showed improved removal of ammonia nitrogen. In the acidified solution, the ammonia nitrogen dissociates more into its NH₄⁺ form, which passes through the membrane with greater difficulty. The permeate formed from the acidified leachate contained only 4.82 mg/L of N_{ammon}, compared to 8.54 mg/L of N_{ammon} in the permeate produced from the un-acidified leachate.

3.2. Effect of humic acids on the separation process

Fig. 2 shows the dependence of the permeate flow on the concentration factor and on the concentration of added humic acids. The decrease of the permeate flow in the batch process at a constant pressure was caused by an increase of osmotic pressure of the solution, and by the formation of membrane fouling. Fig. 2 demonstrates that the permeate flux strongly depends on the amount of added humic acids and on the achieved concentration factor. For example, when 50 mg/L humic acids were added, the permeate flux decreased on average by 18%.

The addition of humic acids increased the concentration of inorganic salts in the permeate. For example, the average rejection decreased by 20% when 50 mg/L humic acids were added. Rejection was related to flux decline. During the separation process, the highest decrease of flux and rejection was observed when a concentration factor of $c_F = 7$ was achieved (Fig. 3).

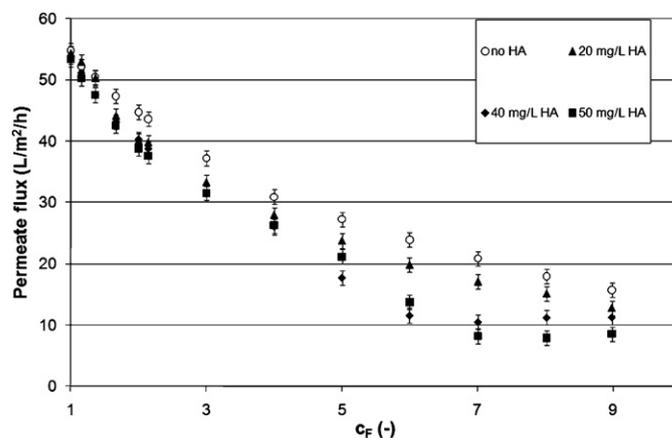


Fig. 2. Effect of added humic acids (HA) concentration on flux performance for RO98pHt membrane in batch mode.

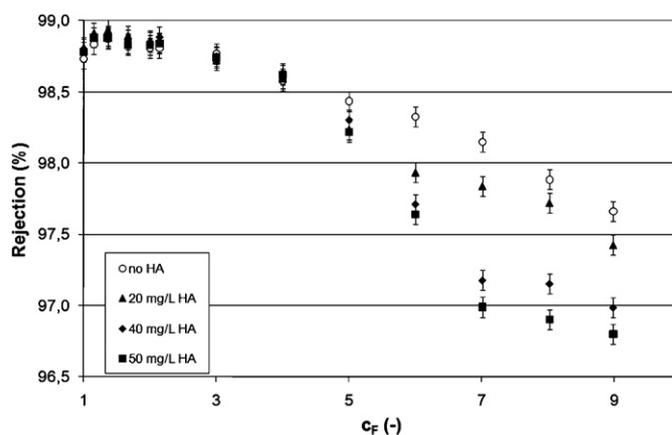


Fig. 3. Effect of added humic acids (HA) concentration on rejection for RO98pHt membrane in batch mode.

4. Conclusions

This study dealt with application of reverse osmosis for hazardous landfill leachate treatment on a pilot scale, followed by membrane fouling experiments studying the influence of humic

acids on the permeate flow and total rejection of leachate components.

The main conclusions for pilot plant experiments 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, which corresponds to 99.3% rejection. 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, which corresponds to 97.3% rejection. Acidification of the leachate from original pH 7.7 to the value of 5.0 by adding HCl resulted in lower concentration of ammonia nitrogen in the permeate (decrease from 8.54 mg/L to 4.82 mg/L). The remaining concentrate accounted for only 6% of the original input volume, when two consecutive stage of reverse osmosis were used. Even at that high degree of concentration, no undesirable precipitation of solution components (which would cause an abrupt decrease in permeate flux) was detected. Except for the high concentration of ammonia nitrogen, the permeate satisfied all the quality requirements stipulated by the contracting authority.

Membrane fouling experiments showed, that the permeate flux and rejection decreased with the increasing concentration of added humic acids leached from oxihumolite, which is scheduled to be deposited on the nearby bioremediation site. 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 $c_F = 10$ was reached. Leaching of wastes containing humic acids may adversely affect the separation efficiency of the other leachate components.

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References

- [1] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard. Mater.* 150 (2008) 468–493.
- [2] K. Linde, A. Jönssone, R. Wimmerstedt, Treatment of three types of landfill leachate with reverse osmosis, *Desalination* 101 (1995) 21–27.
- [3] G. Steven, C. Görller-Walrand, K. Leuven, The use of RO for the treatment of contaminated groundwater and leachate, in: *Proceeding of Euromembrane'95*, University of Bath, 1995, pp. 449–455.
- [4] T.A. Peters, Purification of landfill leachate with reverse osmosis and nanofiltration, *Desalination* 119 (1998) 289–295.
- [5] G. Baumgarten, C.F. Seyfried, Experiences and new developments in biological pretreatment and physical posttreatment of landfill leachate, *Water Sci. Technol.* 34 (1996) 145–152.
- [6] L. Yanping, L. Xiujin, W. Baozhen, L. Shuo, Performance of landfill leachate treatment system with disc-tube reverse osmosis units, *Front. Environ. Sci. Eng. China* 2 (2008) 24–31.
- [7] R. Rautenbach, T. Linn, High-pressure reverse osmosis and nanofiltration, a "zero discharge" process combination for the treatment of waste water with severe fouling/scaling potential, *Desalination* 105 (1996) 63–70.
- [8] C.Y. Tang, Y.N. Kwon, J.O. Leckie, Fouling of reverse osmosis and nanofiltration membranes by humic acid – effects of solution composition and hydrodynamic condition, *J. Membr. Sci.* 290 (2007) 86–94.
- [9] J.D. Ritchie, E.M. Perdue, Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter, *Geochim. Cosmochim. Acta* 67 (2003) 85.
- [10] J. Harmsen, Identification of organic compounds in leachate from a waste tip, *Water Res.* 17 (1983) 699–705.
- [11] J. Artiola-Fortuny, W.H. Fuller, Humic substances in landfill leachates: I. Humic acid extraction and identification, *J. Environ. Qual.* 11 (1982) 663–668.
- [12] J.B. Christensen, D.L. Jensen, C. Gron, Z. Filip, T.H. Christensen, Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater, *Water Res.* 32 (1998) 125–135.
- [13] C. Gron, L. Wassenaar, M. Krogh, Origin and structures of groundwater humic substances from three Danish aquifers, *Environ. Int.* 22 (1996) 519–534.
- [14] Y. Wu, S. Zhou, F. Qin, H. Peng, Y. Lai, Y. Lin, Removal of humic substances from landfill leachate by Fenton oxidation and coagulation, *Process Saf. Environ. Prot.* 88 (2010) 276–284.
- [15] C. Berthe, E. Redon, G. Feuillade, Fractionation of the organic matter contained in leachate resulting from two modes of landfilling: an indicator of waste degradation, *J. Hazard. Mater.* 154 (2008) 262–271.
- [16] Z. Liang, J.X. Liu, J. Li, Decomposition and mineralization of aquatic humic substances (AHS) in treating landfill leachate using the Anammox process, *Chemosphere* 74 (2009) 1315–1320.
- [17] W.S. Ang, S.Y. Lee, M. Elimelech, Chemical and physical aspect of cleaning of organic-fouled reverse osmosis membranes, *J. Membr. Sci.* 272 (2006) 198–210.
- [18] D.L. Rowell, *Soil Science. Methods and Applications*, Longman Scientific and Technical/John Wiley, New York, 1994.
- [19] G.P. Sheng, M.L. Zhang, H.Q. Yu, A rapid quantitative method for humic substances determination in natural waters, *Anal. Chim. Acta* 592 (2007) 162–167.