Desalination and Water Treatment
www.deswater.com

14 (2010) 233–238
February

doi: 10.5004/dwt.2010.1076

Nanofiltration and reverse osmosis of pig manure: Comparison of results from vibratory and classical modules

Sz. Kertész[a]*, S. Beszédes[b], Zs. László[b], G. Szabó[b], C. Hodúr[b]

[a]*School of Environmental Sciences, University of Szeged, Dugonics tér 13, Szeged H-6720, Hungary*
Tel. +36203549618; fax: +3662546034; email: kertesz@mk.u-szeged.hu
[b]*Department of Mechanical and Process Engineering, University of Szeged, Moszkvai krt 5-7, Szeged H-6725, Hungary*

Received 16 July 2009; accepted 3 December 2009

ABSTRACT

The use of membrane technology is a good possibility for the concentration of manure into a small volume that can be transported to the fields. The disposal of manure often requires pre- or post-treatment with respect to environmental legislation. Membrane processes would be a good way to achieve these requirements. In pressure-driven membrane processes, microfiltration and ultrafiltration are usually efficient in concentrating the nutrients associated with particles, such as phosphorus, but for other constituents, e.g. ammonia and potassium, the retention requires nanofiltration (NF) or reverse osmosis (RO). In this study, two different membrane processes, a classical cross-flow (3DTA) and a vibratory shear-enhanced process (VSEP) were compared as regards the reduction of the total volume and the dry matter from pig manure. Two NF and two RO membranes were used. The fluxes were compared during the tests of pretreated manure concentration. Each composite membrane was tested with regard to the membrane, gel layer and porous resistances. It was found that the gel layer was much lower in the case of the VSEP, because of the high shear-enhanced forces on the membrane surface during the experiments. Our results indicated that NF and RO were suitable for pig manure treatment.

Keywords: Manure; Nanofiltration; Reverse osmosis; VSEP; Fouling; Membrane resistance; Gel layer resistance; Total resistance

1. Introduction

Manure mainly consists of water, complex carbohydrates, and nutrients. In the course of effluent treatment, complex carbohydrates can break down into simpler compounds, such as carbon dioxide and water. Manure also contains large quantities of nitrogen, phosphorus and potassium, as well as minor nutrients, trace elements and salts [1]. A range of pathogens (bacteria, viruses and others) too are present in pig manure. The nutrients in manure include the major nutrients found in commercially available fertilizers, including nitrogen, phosphorus and potassium, together with other minor nutrients and trace elements. The salts found in manure mainly involve sodium, calcium, magnesium, chloride, sulfate and carbonate.

Most of the manure produced must be stored in order to minimize the effects on the environment, and one of the major problems of manure storing is the odor problem. Since nitrogen is usually present in ammonium or organic nitrogen form, it is readily converted to ammonia. This is in gas form, and can

*Corresponding author

Presented at the Fourth Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2009), Prague, 7-11 June, 2009.

therefore contribute to the odor problems; it additionally enhances aerosol formation, giving rise to plant and animal health concerns, and it has also been referred to as an indirect greenhouse gas, which has the potential to undergo oxidation into nitrous oxide, which contributes to global warming [2]. Furthermore, phosphorus and nitrogen are culprits in polluting potable water and causing eutrophication [3].

One classical solution for the removal of organic matter is anaerobic digestion. This offers several advantages, such as renewable energy (e.g. methane production), the reduction of pollution and odors, and the recycling of nutrients back into the soil, but transportation costs set a limit to the utilization of the digested effluents [4]. Manure transport to distant fields is generally not profitable, and the volume of the manure should therefore be diminished to reduce the transport costs. One solution via which to achieve this would be the use of membrane processes. The application of membranes for the treatment of manure has increased considerably during the past decade, mainly because of the tightening of environmental regulations [5–7]. For the treatment of wastewaters, fouling is an important phenomenon that limits the applicability of membrane processes. Such fouling can be caused by cake/gel layer formation and inner pore plugging [8]. Gel layer formation is caused by the accumulation of particles at the membrane interface while pore blocking is due to the accumulation of solutes and particles attached to the interior membrane pores. A considerable amount of manure and slurry is produced on animal farms in Europe. The environmental regulations relating to animal husbandry and the elimination of air and water pollution from manure are becoming increasingly stringent [9].

In this study, our aim was to compare the nanofiltration and reverse osmosis of pig manure by a classical cross-flow (3DTA) and a vibratory shear-enhanced process (VSEP). Two NF and two RO membranes' fluxes were compared during the examination tests. Each composite membrane was tested with regard to the membrane, gel layer and porous resistances.

2. Materials and methods

2.1. Pretreatment of manure

Raw manure was collected from the storage ponds of the Pig Mark Farm in Szeged, Hungary. As nanofiltration (NF) and reverse osmosis (RO) require relatively extensive manure pretreatment to prevent membrane fouling, maximize membrane life and increase the flux, centrifugation was carried out before the membrane separation with an instrument (CEPA, Carl Padberg 7630, Germany) operating at 3,000 rpm and a flow rate of 100 s L^{-1} with a 100-μm bagfilter. It was then homogenized with a stirrer (IKA T18-Basic, Ultra-Turrax, Germany) rotating at 21,500 min^{-1} for 10 min.

2.2. Analytical methods

The change in the content of total soluble solids (TSS) was followed with an Atago Palette digital refractometer (PR-101α) with scale range of 0–45 °Brix. Prior to each set of measurements, the instrument was calibrated at 0 °Brix with deionized water. The conductivity was measured with a multi-parameter analyser (Consort C535, Belgium).

2.3. Concentration experiments

All measurements were carried out at 25 ± 2 °C, the feed was thermostated, and the temperature (T) was checked before and after the membrane filter. The applied trans-membrane pressure (TMP) was 25 and 35 bar for NF and RO, respectively. After each run, the membrane was washed with deionized water until the pure water flux (J_W) reached the initial value measured after compaction (±2%). Two different types of NF and two different types of RO membranes were used for the continuous mode concentration tests. Table 1 shows the characteristics and operation conditions of the membranes.

2.3.1. Vibratory shear-enhanced process (VSEP) experimental set-up

The filtration module was a VSEP Series L (New Logic Research Inc., Emeryville, CA), equipped with a single circular membrane of 503 cm^2 (13.5 cm outer radius R_2, 4.7 cm inner radius R_1). The vertical shaft supporting the membrane housing acts as a torsion spring which transmits the oscillations of a lower plate in the base, which is vibrated by an eccentric drive motor. As a result, the housing containing the membrane oscillates azimuthally with displacement amplitude d, which was adjusted to be 25.4 mm (1 inch) on the outer rim at the resonant frequency (F) of 55 Hz. The volumetric flow rate (q_V) was constant, at 200 L h^{-1} in all cases. The module was fed from a thermostatically controlled and stirred 20-L tank by a volumetric diaphragm pump.

2.3.2. 3DTA experimental set-up

The concentrations were carried out on a classical module, Uwatech 3DTA laboratory cross-flow

Table 1
Membrane characteristics and operating conditions

Membrane process	VSEP		3DTA	
Membrane surface	503 cm^2		156 cm^2	
Filtration type	NF	RO	NF	RO
Membrane	NE90	LFC	DL	SG
Membrane configuration	Flat coupon			
Membrane material	TFC polyamide	Thin-film composite (TFC)		
Vendor	Filmtec	Hydranautics	GE Osmonics	GE Osmonics
Operating pressure [bar]	25	35	25	35
Max. allowable pressure [bar]	30	69	41	41
Operating T [°C]	25 ± 2	25 ± 2	25 ± 2	25 ± 2

membrane filter (Uwatech Gmbh., Germany), with the use of flat-sheet standard membranes (Table 1) with a filtering surface area of 156 cm^2. The pressure applied was 25 and 35 bar for NF and RO, respectively. The volumetric flow rate was 500 L h^{-1} and the linear velocity of solution along the surface of membrane 0.4 m s^{-1} in all experiments.

2.4. Calculation methods

The flux (J) was determined via the equation:

$$J = \frac{dV}{dt}\frac{1}{A}\left[\mathrm{Lm^{-2}h^{-1}}\right] \quad (1)$$

where A is the surface area of the filter [m^2], V is the filtration volume [L], t is time [h].

The volumetric concentration ratio (VCR) during concentration of the emulsion was determined:

$$\mathrm{VCR} = \frac{V_{\mathrm{feed},0}}{V_{\mathrm{feed},0} - V_{\mathrm{perm}}}, \quad (2)$$

where $V_{\mathrm{feed},0}$ is the feed volume at the beginning of the operation, and V_{perm} is the permeate volume.

The total resistance (R_{T}) is composed of three resistances:

$$R_T = R_M + R_F + R_G\left[\mathrm{m^{-1}}\right] \quad (3)$$

and

$$J = \frac{p}{\eta(R_M + R_F + R_G)}\left[\mathrm{Lm^{-2}h^{-1}}\right], \quad (4)$$

where R_{M} is the membrane, R_{F} is the porous-fouling resistance and R_{G} is the polarization/gel layer resistance. R_{M} was calculated as

$$R_{\mathrm{M}} = \frac{\Delta p}{J_{\mathrm{W}} * \eta} \quad \left[\mathrm{m^{-1}}\right] \quad (5)$$

where J_{W} is the flux of clear water [L m^{-2} h^{-1}], and η is the viscosity of water at 25 °C. R_{F} can be measured via the pure water flux (J_{W2}), i.e. the following washing of the gel layer from the membrane. R_{F} and R_{G} can be calculated as

$$R_{\mathrm{F}} = \frac{p}{J * \eta} - R_{\mathrm{M}} \quad \left[\mathrm{m^{-1}}\right] \quad (6)$$

$$R_{\mathrm{G}} = \frac{p}{J * \eta} - R_{\mathrm{M}} - R_{\mathrm{F}} \quad \left[\mathrm{m^{-1}}\right], \quad (7)$$

where η is the viscosity of the filtered solution at 25 °C.

The selectivity of a membrane for a given solute was expressed by the average (apparent) retention coefficient (R):

$$R\% = \left(1 - \frac{c}{c_0}\right)100 \quad [\%], \quad (8)$$

where c is the average concentration of the solute in the permeate phase, and c_0 is the concentration of the solute in the bulk solution.

3. Results and discussion

3.1. Fluxes

A comparison of the VSEP and 3DTA systems during concentration of the pretreated manure is illustrated in Fig. 1. During the concentration tests, the VSEP systems yielded a higher flux than the 3DTA systems. There were no significant differences between the permeate fluxes for the VSEP NF and RO systems. In the case of the 3DTA system, J decreased more rapidly in the first few minutes, especially for the NF system; followed by a gentle slope, and finally the curve leveled out at lower values. The initial differences between the VSEP and 3DTA J levels was high (71.06 and 68.48 L m^{-2} h^{-1} for VSEP RO and NF, and

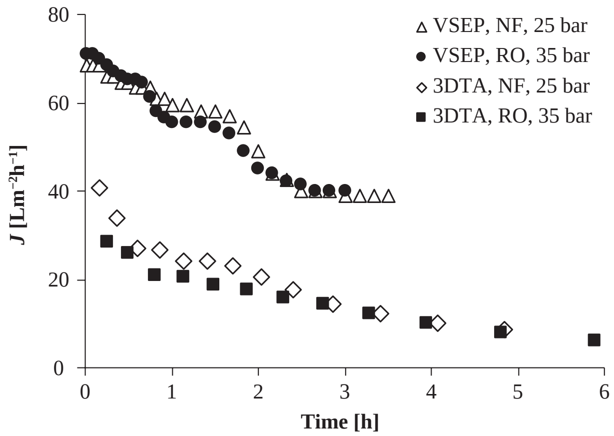

Fig. 1. J vs t during the concentration of manure with the VSEP and 3DTA systems. (VSEP parameters: $T = 25°C$, $q_V = 680$ L h^{-1}, $F = 55$ Hz; 3DTA parameters: $T = 25°C$, $q_V = 500$ L h^{-1}).

28.6 and 40.6 L m^{-2} h^{-1} for 3DTA RO and NF, respectively). The 3DTA NF system J level decreased very rapidly in the first few minutes, followed by a slower fall, and finally a quite constant steady-state value was observed (from 40.06 L m^{-2} h^{-1} to 8.6 L m^{-2} h^{-1}). The initial large drop in J was caused by concentration polarization, which is generally unavoidable in membrane processes. Furthermore, the gradual build-up of solute particles near the membrane surface also decreased J. This may lead to the formation of a gel layer. The solute particles may also block the membrane pores and thus alter the permeability and retention parameters. These changes were more recognizable for the 3DTA systems, because the high vibration in VSEP systems creates very high shearing energy at the surface of the membrane and near the pores.

J in the 3DTA NF system was higher than that in the RO system during the first 3 h, after which the curves continued almost identically.

Fig. 2 depicts the VSEP flux reduction ratio (J/J_0) and the TSS concentration of the retentate (c_R) as functions of VCR. During the progress of the concentration with increasing VCR J/J_0 decreased and c_R increased. It seems that the particles are not so strongly attached in the pores of the membrane; the vibration amplitude therefore decreased the gel layer formation and the fouling occurred later.

As the experiment progressed, c_R increased from 3.1 to 10.0 and to 13.6 °Brix and at the end of the run J had dropped to 38.8 and 40.1 L m^{-2} h^{-1} (Fig. 1), respectively. In addition, VCR increased from 1 to 1.6.

The retentate TSS content for the 3DTA system could not be shown continuously in a diagram, because it could not be measured during the experiment, but only at the end of the tests. It reached 6.7 °Brix and 8.5 °Brix for NF and RO, respectively. Moreover, a higher VCR was measured at the end of the test (2.8 for RO and 3.2 for NF).

3.2. Retentions

The retentions of the TSS content were calculated via Eq. (8) from the differences between the TSS levels of the permeates and the feed (Fig. 3). Higher retentions were observed for the VSEP systems. For NF 93.59% vs 58.82% retention for 3DTA and for RO 95.14% vs 87.94% retention for 3DTA was calculated.

Fig. 4 shows the membrane retention results. In the NF experiments (Fig. 4a), the VSEP TFC polyamide

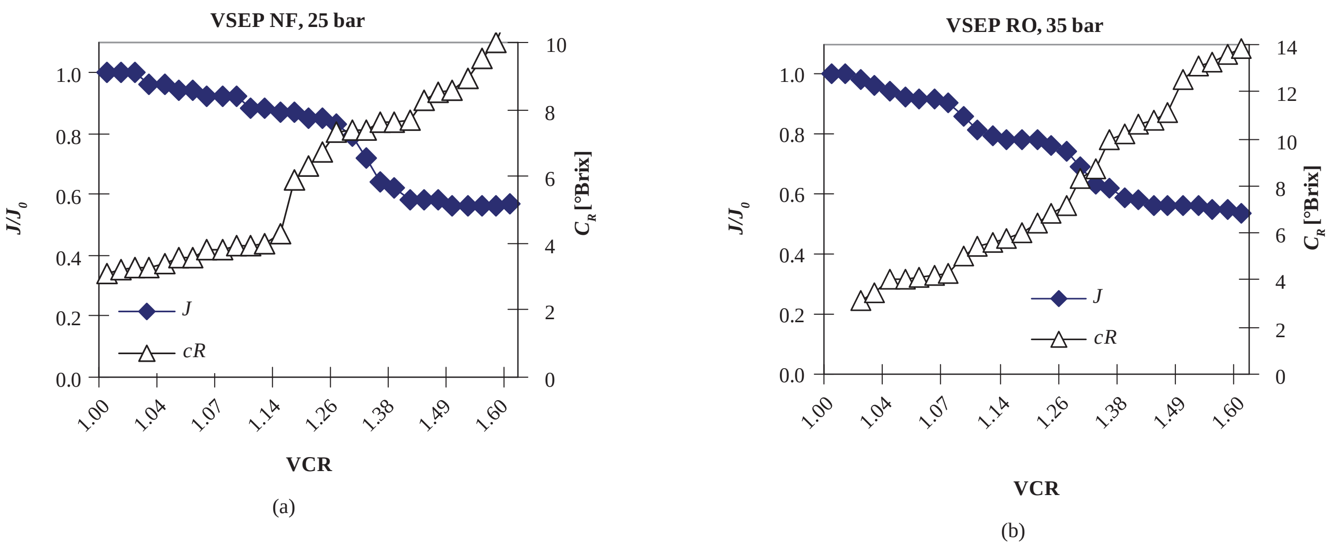

Fig. 2. J/J_0 and c_R vs VCR during concentration of manure with the VSEP NF (a) and VSEP RO (b) systems.

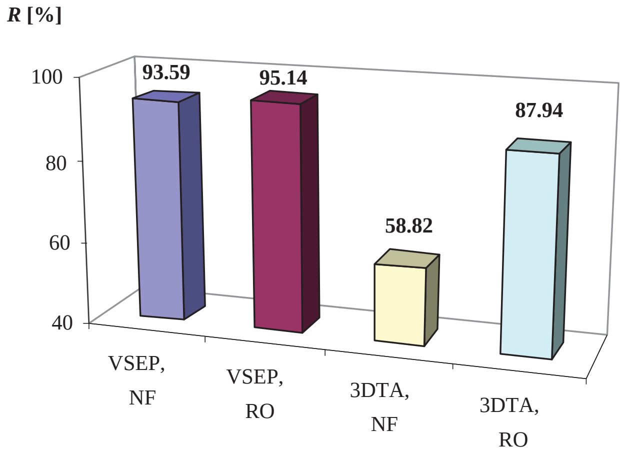

Fig. 3. Comparison of the average TSS R values with different membranes.

membrane retention fell from 100 to 88% and the classical module TFC membrane retention decreased from 63 to 39%. In the RO experiments (Fig. 4b), the VSEP TFC membrane retention fell from 100 to 94%, and the classical module TFC GE membrane retention decreased from 94 to 86%.

3.3. Resistances

The total resistance of membrane filtration (R_T) consists of the membrane resistance (R_M), the resistance of the inner porous membrane fouling (R_F) and the gel layer resistance (R_G) referring to the concentration polarization and the formation of a gel layer on the surface of the membrane [10]. This may lead to blockage of the membrane, thereby reducing its trans-membrane J value.

From Eqs. (3–6), the individual R values could be calculated. The results are illustrated in Table 2 for the experiments performed with the four membranes tested. The highest percentage contributions of R_M were observed for the VSEP NF and RO systems, i.e. almost 2 times higher than for the 3DTA membrane. Higher R_M for the VSEP NF and RO systems as values were observed compared to R_F and R_G. Further, for the 3DTA NF system, R_T was almost 5 times higher (27.78 vs $5.56{}^*10^{-13}$ m^{-1}), and for the with 3DTA RO system it was more than 3 times higher (38.1 vs $11.67{}^*10^{-13}$ m^{-1}) than for the VSEP systems. The differences were especially pronounced in the cases of R_F and R_G. The VSEP results revealed lower values for R_F and R_G. The highest R_F ($9.67{}^*10^{-13}$ m^{-1}) and R_G ($15.75{}^*10^{-13}$ m^{-1}) values were obtained for the 3DTA RO and NF membranes, respectively. It should be noted that R_F was one order of magnitude lower than R_M except for the 3DTA NF system. On the other hand, in the VSEP systems, R_F did not seem to be a determining factor as concerns J, because it was an order of magnitude lower than R_M. Furthermore, in the VSEP RO system, R_F was much lower than R_G, and had practically no influence on the J value of manure. It was found that the gel layer was much thinner in the case of the VSEP systems.

During manure NF with the 3DTA system, R_G was higher than R_F. The concentration polarization could be minimized by appropriate selection of TMP or/and the feed tangential velocity, i.e. the shear stress. When the VSEP system was used, R_T was reduced by 20% and R_F was larger than R_G; the measured R_G was 1.8%, and R_F was 11.9% of that measured with the 3DTA system.

4. Conclusions

Two different membrane processes, classical 3DTA and VSEP, were compared for reduction of the total volume and TSS content of pig manure pretreated by

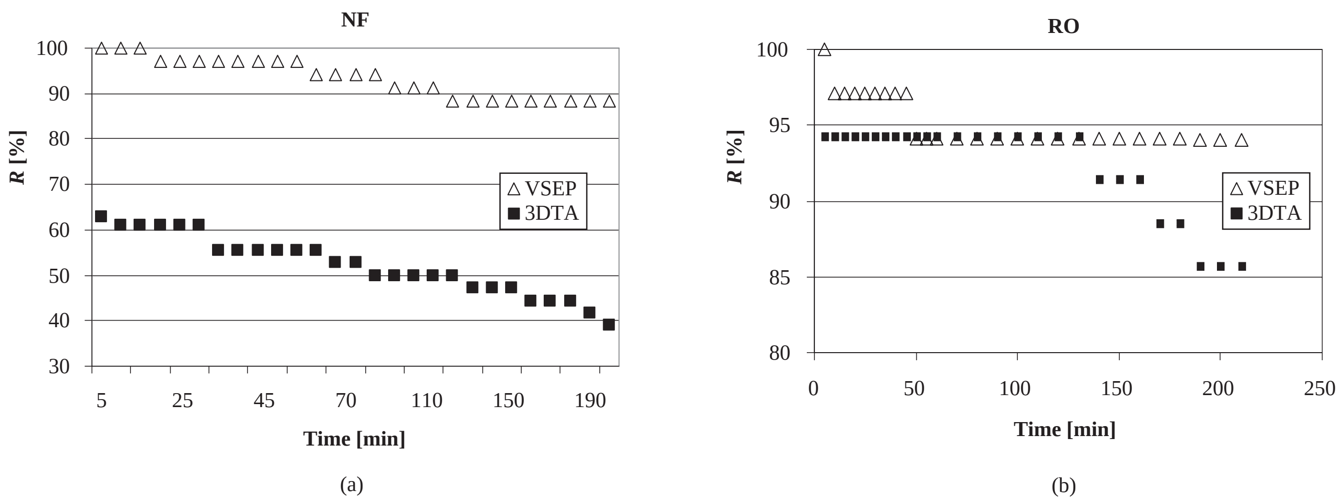

Fig. 4. Changes in TSS R values with t during NF (a) and RO (b) concentration of manure.

Table 2
Calculated total resistance, R_T, and its contributions

System	Membrane	R_T*10^{-13} [m^{-1}]	R_M/R_T*100 [%]	R_F/R_T*100 [%]	R_G/R_T*100 [%]
3DTA, NF	DL	27.8	31.2	12.1	56.7
3DTA, RO	SG	38.1	49.9	25.4	24.7
VSEP, NF	NE90	5.6	87.2	7.7	5.1
VSEP, RO	LFC	11.7	75.9	6.6	17.5

NF or RO. Since fouling induced by different complex carbohydrates, and nutrients in pig manure is a major challenge limiting the use of NF and RO in many wastewater treatment applications, R_M, R_G and R_F were also calculated and compared.

These resistances could be reduced (especially R_F and R_G) by using torsion vibration of flat-sheet membranes to induce high shear rates at the membrane surface.

The R_T levels could be reduced by vibratory shear force to 20% and to 31% for NF and RO, respectively. Vibration substantially reduced R_F and R_G and increased the practical recovery.

Acknowledgements

The authors are grateful to the National Research and Technology Institute (NKTH), Oszkár Asbóth Innovation Programme for Pull-Sectors (DAMEC_09) and RET-07/2005 project.

Nomenclature

A	surface area of the filter [m^2]
Δp	pressure difference between the two sides of the membrane [bar]
$\Delta\pi$	osmotic pressure difference across the membrane [Pa]
c	concentration of the solute in the permeate phase [m/m %]
c_0	concentration of the solute in the bulk solution [m/m %]
c_R	total soluble solid content of retentate [°Brix]
F	frequency [Hz]
J	permeate flux [L m^{-2} h^{-1}]
J/J_0	flux reduction ratio
J_w	pure water flux of the clean membrane [L m^{-2} h^{-1}]
NMWL	nominal molecular weight limit [Da]
NaOH	sodium hydroxide
NF	nanofiltration
η	viscosity [Pas]
q_V	volumetric flow rate [L h^{-1}]
R	membrane retention [%]
R_G	resistance of the gel/cake layer [m^{-1}]
R_F	internal porous fouling resistance [m^{-1}]
R_M	resistance of the clean membrane [m^{-1}]
R_T	total resistance of the system [m^{-1}]
RO	reverse osmosis
t	time [h]
T	temperature [°C]
TFC	Thin-film composite
TMP	trans-membrane pressure [bar]
TSS	total soluble solids [°Brix]
VCR	volumetric concentration ratio
VSEP	vibratory shear-enhanced process

References

[1] G. Johnson, B. Culkin and L. Stowell, Membrane Filtration of Manure Wastewater, Technical Article, August 2004.
[2] M. Ferm, A. Kasimir-Klemedtsson, P. Weslien and L. Klemedtsson, Emission of NH_3 and N_2O after spreading of pig slurry by broadcasting or band spreading, Soil Use Manag., 15 (1999) 27–33.
[3] R.J. Zeng, R. Lemaire, Z. Yuan and J. Keller, Simultaneous nitrification, denitrification, and phosphorus removal in a labscale sequencing batch reactor, Biotech. Bioeng., 84 (2003) 170–178.
[4] D. Karakashev, J.E. Schmidt and I. Angelidaki, Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure, Water Res., 42 (2008) 4083–4090.
[5] M. Mondor, L. Masse, D. Ippersiel, F. Lamarche and D.I. Masse, Use of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure, Biores. Tech., 99 (2008) 7363–7368.
[6] L. Masse, D.I. Masse and Y. Pellerin, The use of membranes for the treatment of manure: a critical literature review, Biosyst. Eng., 98 (2007) 371–380.
[7] C.H. Burton, The potential contribution of separation technologies to the management of livestock manure, Liv. Sci., 112 (2007) 208–216.
[8] R. Fugere, N. Mameri, J.E. Gallot and Y. Comeau, Treatment of pig farm effluents by ultrafiltration, J. Membr. Sci., 255 (2005) 225–231.
[9] L. Thörneby, K. Persson and G. Tragardh, Treatment of liquid from dairy cattle and pigs using reverse osmosis, J. Agri. Eng. Res., 73 (1999) 159–170.
[10] Zs. László, Sz. Kertész, E. Mlinkovics and C. Hodúr, Dairy waste water treatment by combining ozonation and nanofiltration, Sep. Sci. Tech., 42(7) (2007) 1627–1637.
[11] D.M. Krstic, W. Höflinger, A. Koris and Gy. Vatai, Energy-saving potential of cross-flow ultrafiltration with inserted static mixer: application to an oil-in-water emulsion, Sep. Pur. Tech., 57 (2007) 134–139.