MICROFILTRATION NANOFIBROUS MEMBRANE FOR WASTEWATER TREATMENT

Jaroslav Lev[a], Marek Holba[a,b], Michal Došek[a,c], Libor Kalhotka[c], Lenka Detvanová[c], Lenka Dostálová[c], Jitka Přichystalová[c], Ivo Vincent[d], Dušan Kimmer[d]

[a] *ASIO spol. s r.o., Kšírova 552/45, 619 00 Brno, Czech Republic, lev@asio.cz, dosek@asio.cz*

[b] *Institute of Botany, Academy of Science of the Czech Republic, v.v.i., Lidická 25/27, 657 20 Brno, Czech Republic, holba@asio.cz* [b]

[c] *Faculty of Agronomy, Mendel University in Brno, Zemědělská 1, 613 00 Brno, Czech Republic, libor.kalhotka@mendelu.cz, lenka.detvanova@gmail.com, lenka.dostalova@mendelu.cz, jitka.prichystalova@mendelu.cz*

[d] *SPUR, a. s., tř. T. Bati 299 Louky, 764 22 Zlín, Czech Republic, KimmerDusan@spur.cz*

Abstract

Production of nanofibers by electrospinning methods offers the potential of new high-flux filtration materials. High porosity together with small pore size include some of many advantages of nanofiber materials. Wide range of studies focused on usage of nanofiber materials for wastewater treatment has been published [1], [2], [3]. Our work is focused on the application of microfiltration nanofiber material (SpurTex® MF) in membrane bioreactors (MBR). The main aim of this work was to separate the activated sludge and removal of microbial water contamination. The microfiltration nanofiber based membrane with a medium pore size of 0.30 ± 0.1 microns was prepared from polyurethane (PU) nanofibers using the electrospinning multinozzle device SpinLine 120. This material was used to design pilot flat sheet unit of membrane module with a membrane surface of 3.6 m^2. Long-term filtration efficiency and operating parameters of the module were monitored in real conditions of municipal wastewater treatment plant. The results showed good separation ability of nanofiber based membranes and long-term endurance in real conditions.

Keywords:

Electrospun nanofibers, wastewater, filtration, bacteria, membrane bioreactor,

1. INTRODUCTION

Membrane bioreactor technique is one of the new yet swiftly maturing technologies in the waste water treatment industries. MBR reactors using biological processes, as in the existing biological treatment plants, but are supplemented by a separation unit which separates the active sludge, fine particles and bacteria. These technologies achieve higher quality clean water and allow its further use. Conventional ubiquitous technologies are estimated to be replaced by MBR systems in the coming years, owing to low operation and maintenance costs of MBR systems. MBR sales are being driven by increasingly strict legislation concerning discharge quality and recycling levels [4]. Collectively, they are all pushing for better sanitation and water resource rehabilitation through effective wastewater treatment and reclamation means.

Growing popularity of MBR system applications is likely to boost the product demand over the forecast period. In terms of volume, the municipal wastewater treatment application market is likely to grow at a CAGR (Compound Annual Growth Rate) 21.7% from 2013 to 2019. [4, 5].

In connection with the growing interest in MBR systems is the development of new filter materials, which would still improve the properties of existing technologies. Promising areas represent nanostructured materials. One of these materials can be electrostatically spun polymer nanofiber structure (electrostatic nanofibers structures). These structures have a high porosity with small pore size [6, 7, 8]. Manufacturing method of electrospinning is currently experiencing a great development, and nanofiber structures are becoming more common and affordable. In several earlier studies were conducted laboratory and pilot plant tests with nanofiber materials and proven usefulness in the field of water treatment [9, 10]. These studies and previous experiments, this study builds. The paper presents the design of MBR test module and tests carried out in the field. The result of the study is to evaluate the applicability of the produced nanofiber material for the production of modules for membrane bioreactors.

2. EXPERIMENTAL

2.1 Materials

A modified polyurethane solution in dimethylformamide (DMFA) for electrostatic spinning was prepared from diisocyanate, polyesterdiol, 1,4-butanediol and phthalocyanine containing amino or hydroxyl group at the temperature of 90 °C for a time period of 6 hours. Per partes method of synthesis was used. The solution was diluted with DMFA to a viscosity of 1.3 Pa.s and conductivity was increased to 150 μS/cm.

2.2 Preparation and characterization of electrospun nanofibrous membrane

Nanofiber layers were prepared from the polymeric solutions via commercially available SpinLine 120 equipment (SPUR a.s., Zlín, Czech Republic) using nanofibres forming jets. The experimental conditions were as follows: 28% relative humidity, 23 °C temperature, 75 kV voltage applied to the PU solution, 210 mm distance between electrodes and speed of supporting textile collecting nanofibres 0.3 m/min. The nanofibers were collected on surface treated polyester fabric with weight 50 g/m^2.

Nanofibre-based filter prepared by the electrospinning process was characterized by a scanning electron microscope (SEM, Vega 3, Tescan, Czech Republic). Pore size distribution, average pore size value and maximum pore size measurements were analyzed in accordance with ASTM F316 – 03 [11]. Parameter of used material is summarized in Table 1.

Table 1 Parameters of used material SpurTex® MF

Membrane material	PU 1)
Support material	PET 1)
Nominal pore size [μm]	0.3 ± 0.10
Water flux [L/(m²·h)]	> 500 2)
Thickness [μm]	250 - 300
Area weight of nanofibers layer [g/m^2]	2.82

1) PU – polyurethane, PET – Polyethylene terephthalate

2) Test conditions: after 1 hour of distilled water filtration at 7.5 kPa, 23 °C

.2.3 Membrane module specification

Membrane module was composed from 15 flat sheet membranes with nanofibrous material. The membrane was glued and screwed to the frame. All the membrane outlets are directed into one common output. Aerating elements serving to scour the membranes are placed at the bottom of the module. The assembled membrane module is shown on Fig.1, the module parameters are given in Table 2

Fig. 1: Pilot test apparatus

Table 2: Membrane module specification

Membrane module dimensions H x W x D [m]	1.17 x 0.76 x 0.48
Dimensions of membrane H x W [m]	0. 6 x 0. 2
Number of membranes [pcs]	15
Total membrane area [m^2]	0.24
Total membrane module area [m^2]	3.6

2.3 Experimental setup

Before running test was apparatus sterilized by NaClO solution before the experiment. Pilot testing membrane module was carried out in the reservoir of the activated sludge sewage 1100 PE. The membrane module was anchored in the aeration tank. Permeate was pumped through a membrane pump (RM-ECO P10-2.3, 24V) to the backwash tank. Filtrate was recycled from the backwashing tank into the overflow tank. We measured intake manifold pressure and flux. Values were recorded using a PLC (programmable logic controller) to the memory card. To increase the effect of sanitation of the filtrate was irradiated with UVC (Atman UV-9W). To reduce fouling system was used backwashing every 5 minutes. Suction pump was turned off and opens the three-way valve, which ceded portion of the filtrate from the storage tank back into the intake system and membranes. The amount of liquid used for flushing flow was subtracted (flow meter BONEGA TA / 13). Shut-off break for pumping was set to 2 minutes; the backwash lasted 30 seconds in never-ending loop. The amount of permeate used for flushing was measured and recorded. Samples of 100 mL of the filtrate prior to UV irradiation, after the UV irradiation and from the storage tank were collected and subjected to microbiological analyses. Samples were taken at weekly intervals. The culturable microorganisms at 22 ˚C and 36 ˚C were enumerated by inoculation in a PCA (Biokar Diagnostics, France) for 48 and 72 hours. Coliform bacteria were detected and enumerated in a Endo Agar (Merck KGaA, Germany) at 37 °C for 72 hours. Every sample was duplicated. The culturable microorganisms were enumerated by inoculation in nutrient agar culture medium. Intestinal enterococci grown on Slanetz Bartley Agar (Merck KGaA, Germany) for 72 h at 36 ˚C, thermotolerant coliform bacteria on mFC Agar (Merck

KGaA, Germany) for 18-24 h at 44 ˚C.The duration of the experiment was 84 days. Wiring diagram with nanofibre membrane module is shown in Figure 3.

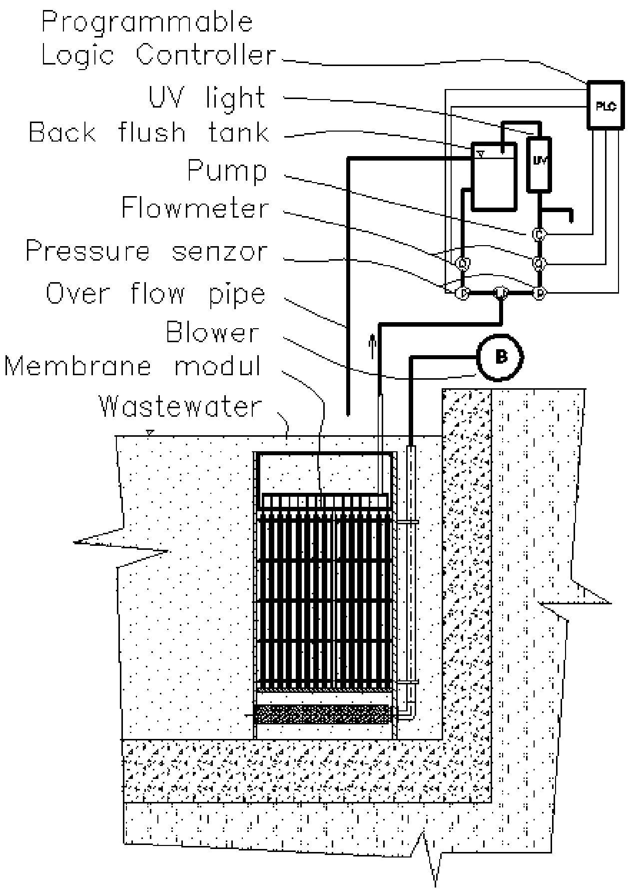

Fig. 3: Pilot test apparatus

3. RESULTS AND DISCUSSION

This article follows on previous laboratory and semi-pilot tests that showed good filtering capabilities of nanofiber layers [10, 12, 13]. The tests described in this article were conducted to evaluate usability of nanofiber materials for wastewater treatment in a membrane bioreactor. Operating parameters (pressure on the membrane, flow) and quality of treated water were monitored during the tests. Figure 4. show the progress of trans membrane pressure (TMP) and flow membrane module during the experiment. There was observed gradual clogging of the filter material during the reporting period (84 days). During the reporting period (84 days) was observed gradual clogging of the filter material. The initial conditions of flow 35 L/h/m^2 at 14 kPa TMP decreased to 12 L/h/m^2 and TMP increased up to 0.76 kPa. We assume that the main cause of reduced flow was biofouling, due to the clogging of nanofiber structures with small particles [14]. In a similar study by Hyun-Chul Kim [15], where experimentally membrane module with 15 pcs PMMA-PVDF membrane microfiltration nanofibre materials with mean pore size of 0.45 micron was used, for pilot testing refining wastewater. The authors achieved a constant flux of 30 L/m^2/h TMP increase from the initial value of 7 kPa to 23 kPa after 18 days of operation without backwashing. In our case occurred after 20 days of TMP increase to about 40 kPa despite the backwash. High TMP causes faster fouling, especially in conditions with higher MLSS. The literature indicates that the MBR are suitable for MSLL in the maximum range 10 to 15 g·L^{-1} [19].The concentration MLSS in the activated sludge tank during the experiment was 16-20 g·L^{-1}.

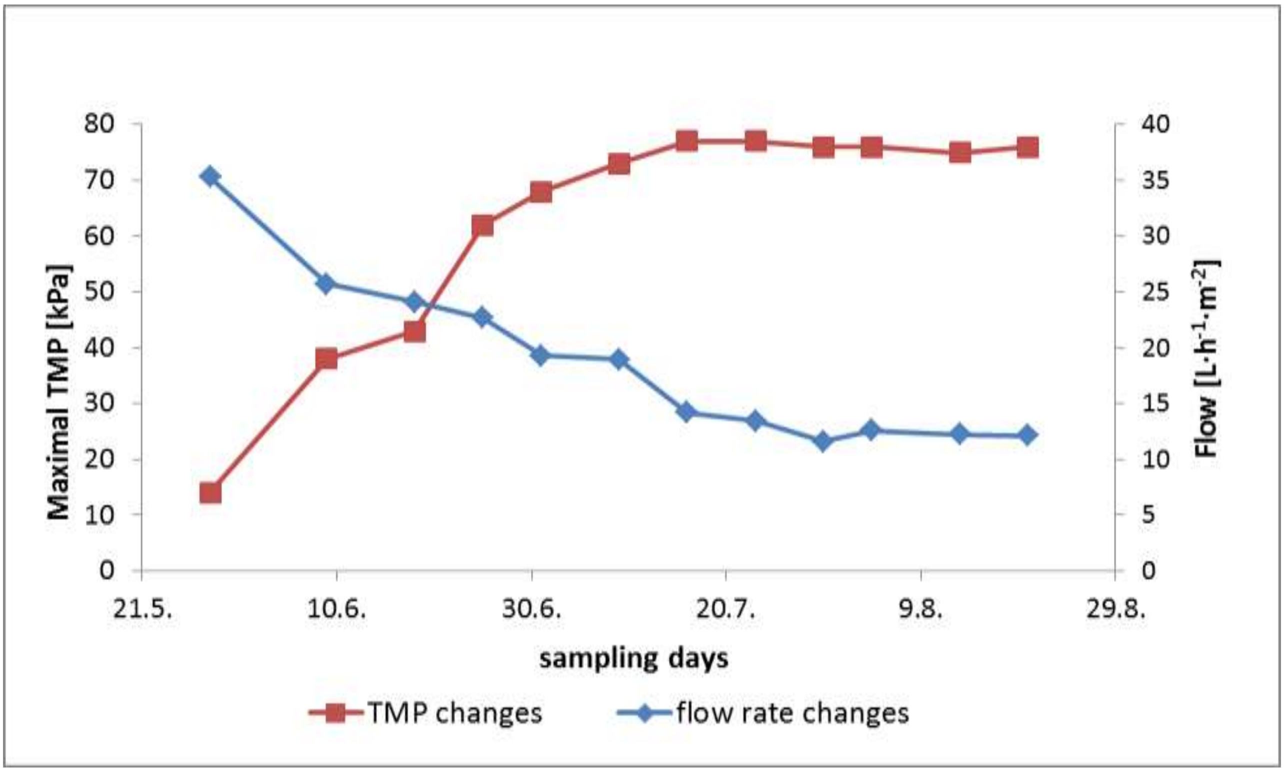

Fig. 4: Pressure and filtration velocity changes during Pilot run

The quality of the treated water was continuously monitored in the filtrate, the filtrate treated with UV and waste water. Values of microbial contamination of the filtrate, the filtrate after UV and wastewater are shown in Fig.5.

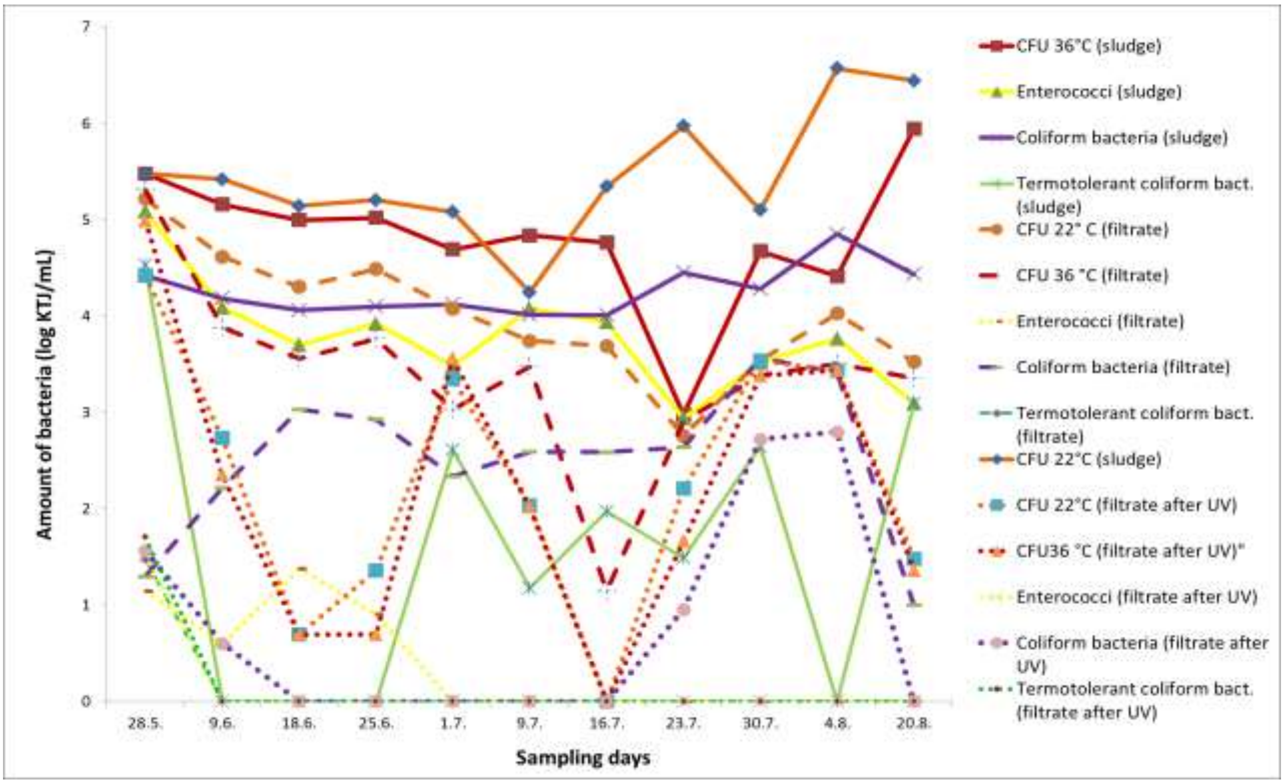

Fig. 5: Monitoring of the microorganisms in activated sludge and in filtrate

There has been a decrease of 1-3 CFU/mL log removal after filtration. These results are comparable to our previous values of the semi-pilot testing in activated sludge [16]. Similar values when using microfiltration PA (Polyamide) nanofiber membranes with a mean pore size of 0.4 micron in laboratory tests indicate Bjorge [17] the log removal of 2.24 CFU/mL of culturable organisms at 37 °C and Daels [9] log removal 1.3- 3.2 CFU/mL *S. aureus* with nanofibre membranes. Higher values were achieved only after functionalization with different functionalizing agents.

UV light was used to increase microbial purity of the filtrate and to evaluate possible water reuse. The reductions of bacterial contamination show Fig. 5. If comparing activated sludge to the filtrate, values of the bacterial contamination are reduced by 2 log removal CFU/mL, and in some case such *coliform bacteria*, enterococci, to zero. Comparison with the legislative requirements in the Czech Republic showed, that the average value of microbial contamination meet the government direction n. 416 / 2010 [18] for emissions standard for treated wastewater into groundwater (500 CFU/mL *E. coli*, 400 CFU/mL *Enterococcus*).

Our pilot tests confirm the usefulness of nanofiber membrane systems in Full-scale. Average flow rate 30 $L \cdot h^{-1}$ was measured with a MBR module (membrane area 3.6 m^2) at the end of the experiment. It means 720 liters per day, which corresponds approximately to the needs of the 5 - members household.

Prior to the introduction of a similar system in practice will still need to verify the long-term reliability and durability of nanofiber materials. It is also necessary to compare the results more in detail with commercial membranes, their parameters and also to test the possibility of regeneration after clogging. These experiments and testing of antifouling modifications of membranes will be part of our future work.

CONCLUSIONS

Pilot testing of nanofiber membrane module demonstrated long-term stability of the filtration process in activated sludge and showed the applicability in real-world conditions at the wastewater treatment plant. Microbial contamination of samples of the filtrate reached log removal 2 CFU/mL. Filtration in combination with UV irradiation resulted in a reduction of microbial contamination under required legislative standards. These results supported our assumptions to use nanofibre membranes in membrane bioreactor. Regeneration, optimization and antifouling surface treatment will be another step to increase the competitiveness of nanofiber membranes for water treatment.

ACKNOWLEDGEMENTS

This study was supported and financed by the Technology Agency of the Czech Republic n. TA01010356.

REFERENCES

[1] RAMAKRISHNA S., KAZUTOSHI F., TEO W. E., LIM T. C., MA, Z., An Introduction to Electrospinning and Nanofibers, Singapore: World Scientific Publishing Co. Pte. Ltd., 2005

[2] GOPAL R., KAUR S., MA Z., CHAN C., RAMAKRISHNA S., MATSUURA T., Electrospun nanofibrous filtration membrane, *Journal of Membrane Science*, 2006, vol.281, p.581-586.

[3] DECOSTERE B., DAELS N., DE VRIEZE S., DEJANS P., VAN CAMP T., AUDENAERT W., HOGIE J., WESTBROEK P., DE CLERCK K., VAN HULLE W.H.S., Performance assessment of electrospun nanofibers for filter applications, *Desalination*, 2009, vol. 249, p. 942–948.

[4] BARHATE R.S., LOONG CH. K., RAMAKRISHNA S., Preparation and characterization of nanofibrous filtering media, *Journal of Membrane Science,* 2006,vol. 283, p. 209–218.

[5] MADAENIS. S. The application of membrane technology for Water disinfection, *Water Resources*, 1999, Vol. 33, No. 2, p. 301-308,

[6] Membrane Bioreactor (MBR) Systems Market By Configuration (Sidestream And Submerged) For Product (Hollow Fiber, Flat Sheet And Multi-Tubular Systems) In Applications (Municipal Wastewater And Industrial

Wastewater) - Global Industry Analysis, Size, Share, Growth, Trends And Forecast, 2012 - 2019. [online]. [cit. 2014-09-12]. availably: http://www.transparencymarketresearch.com/membrane-bioreactor-mbr-market.html

[7] Membrane Multiplier: MBR set for Global Growth. [online]. [cit. 2014-09-12]. availably: http://www.waterworld.com/articles/wwi/print/volume-27/issue-2/regulars/creative-finance/membrane-multiplier-mbr.html

[8] BOTES M., CLOETE T.E., The potential of nanofibers and nanobiocides in water purification. *Critical Reviews in Microbiology*, 2010,vol. 36, p. 68–81.

[9] DAELS N., DE VRIEZE S., SAMPERS I., DECOSTERE B., WESTBROEK P., DUMOULIN A., DEJANS P., DE CLERCK K., VAN HULLE S.W.H., Potential of a functionalised nanofibre microfiltration membrane as an antibacterial water filter, *Desalination*, 2011, vol. 275, p. 285-290.

[10] LEV J., HOLBA M., KALHOTKA L., MIKULA P., KIMMER D., Experimental study on bacteria removal from artificial and real wastewater by nanofibrous filters, *Proc. of Int. Conf. NANOCON 2012*, Brno, Czech Republic, 2012, 23-25. Oct. p.120–126

[11] ASTM F316 – 03 Standard Test Methods for Pore Size Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test

[12] LEV, J., HOLBA, M., DOŠEK, M., KALHOTKA, L., MIKULA, P., KIMMER, D., A novel electrospun polyurethane nanofibre membrane – production parameters and suitability for wastewater (WW) treatment Water, Science & Technology, 2014, vol 69, No 7, p. 1496–1501

[13] LEV J., HOLBA M., DOSEK M., KALHOTKA P., KIMMER D., Nano-and microfibrous composites for water filtration application, *Proc. of Int. Conf. IWA Symposium on Environmental Nanotechnology 2013, Proceedings, Apr. 24-27.2013*, Nanjing. China

[14] DREWS, A. (2010) Membrane fouling in membrane bioreactors—Characterisation, contradictions, cause and cures, Journal of Membrane Science 363, 1-28.

[15] KIM, H.CH, CHOI, B.G., NOH, J., SONG, K.,G., LEE, S., MAENG, S.,K., Electrospun nanofibrous PVDF–PMMA MF membrane in laboratory and pilot-scale study treating wastewater from Seoul Zoo Desalination (2014), 346, 107–114

[16] LEV, J., HOLBA, M., DOŠEK, M., KALHOTKA, L., KIMMER, D., Can nanofibers replace current microfiltration materials? *Proc. of Int. Conf. NANOCON 2013*, Brno, Czech Republic, 2013, 16-18. Oct.

[17] BJORGE D., DAELS N., de VRIEZE S., DEJANS P., van CAMP T., AUDENAERT W., HOGIE J., WESTBROEK P., de CLERCK K., and van HULLE S.W.H., Performance assessment of electrospun nanofibres for filter applications, *Desalination* 2009, 249, p.942 – 948

[18] Government direction n. 416 / 2010 Standard for emissions of treated wastewater into groundwater

[19] JUDD, S., JUDD, C., The MBR Book, Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment,(2012), ISBN: 978-1-85617-481-7