

DETERMINATION OF ORGANOCHLORINATED PESTICIDES BY ELECTROSPUN POLYETHERSULFONE NANOFIBRES

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Abstract

There is an enormous scientific effort devoted to environmental problems solutions based on new and nanostructured materials. Our study follows this trend and contributes to the green analytical chemistry approach. Specifically, it further develops the idea of using nanofibrous sorbents for solid phase microextraction (SPME) as a green technique of pollutant determination.

Nanofibres of polyethersulfone (PES) were successfully prepared by needle electrospinning and fixed on a steel wire SPME assembly. The basic properties of the prepared nanofibres were determined by thermogravimetry (TGA) and scanning electron microscope (SEM). Analytical performance of prepared fibres was compared with common commercially available SPME fibre - 100 µm polydimethylsiloxane (PDMS) in the headspace SPME (HS-SPME) mode of gas chromatograph coupled with tandem mass spectrometer (GC/MSMS). Headspace solid phase microextraction (HS-SPME) is a modern analytical technique for sample introduction into gas chromatographic systems. The HS-SPME technique combines extractive sorption (enrichment) of targets to be quantified with ongoing thermal desorption and injection to the GC system.

Obsolete organochlorinated pesticides (OCP) as HCH, DDT, chlordane, heptachlor, endosulfan, endrin and their transformation products were selected as model analytes in water matrix. With these pollutants, a set of experiments was conducted to proof the effect of key SPME method conditions: extraction time, extraction temperature and sample salinity on OCP MSMS response. PES-nanofibers based SPME assembly prototype comes out to be quite comparable with PDMS fibres under low-salinity conditions and it behaves as expected. Longer extraction times and higher extraction temperatures give higher OCP MSMS response. Even if PDMS fibre performed significantly better for HCH isomers under high salinity conditions, nanofibrous SPME geometry deserves further research as it brings promisingly sensitive OCP MSMS response.

Keywords: Solid phase microextraction, organochlorinated pesticides, electrospun, nanofibres, polyethersulfone, salting out, extraction time, extraction temperature

INTRODUCTION

SPME is modern analytical technique which is a fast, solvent-free alternative to conventional sample extraction methods [1]. This method combines extractive sorption of the targets analytes to be quantified with followed heat desorption and sample injection to the gas chromatographic systems. In the headspace solid phase extraction mode (HS-SPME), the analytes establish equilibrium among the sample matrix, the headspace above the sample and a polymer-coated fused fibre (the most common type of the fibres).

Organochlorinated pesticides are routinely determined by measuring HS-SPME coupled with gas chromatography [2]. Also determination of organochlorinated pesticides are an object of material research, using graphene-coated, calix[4]arene and single-walled carbon nanotube fiber coating for SPME are reported [3,4,5]. Polyethersulfone nanofibers can be also used to removal of endocrine disruptors from water [6]. In these days, PES nanofibers had most used for production of special membranes [7,8]. Currently, there is no published article that investigate using polyethersulfone nanofibers as sorbent for analytical extraction.

In our study, the polyethersulfone (PES) has been selected as a suitable material for analytic extraction due to high thermal stability and mechanical resistance. Nanofibres were produced by needle electrospinning from prepared polymeric solution. Lab-made SPME fibres were prepared by a rotation of stainless SPME plunger inside the fresh stream of PES nanofibers.

OCP were chosen as model pollutants for evaluation of sorption properties of prepared lab-made polyethersulfone SPME fibre and commercial 100 µm PDMS fibre. These compounds are synthetic pesticides widely used all over the world in the second half of 20th century. They belong to the group of chlorinated hydrocarbon derivatives, which had vast application in the chemical industry and in agriculture. They are also known for their high toxicity, slow degradation and bioaccumulation. There are several sites contaminated with OCP in the Czech republic. To study OCP environmental fate a fast, sensitive and green analytical technique needed.

1. MATERIALS AND METHODS

Lab-made SPME fibres were assembled from a stainless steel capillary and wire (Teseco). Plastic parts were printed by 3D-printer using RDG810 polymer (VeroClear). Polyethersulfone (**Figure 1**) was obtained from Sigma-Aldrich (3 mm granule, clear amber) and it was dissolved overnight in a mixture of dimethylformamide/tetrahydrofuran (Sigma-Aldrich) 80:20 into 30 % w/w solution.

Prepared polymeric solution was pumped with flow 10 ml·h⁻¹ into the needle of electrospinner. The collector electrode was subjected to 20 kV voltage. The relative humidity 45 - 55 % and temperature 25 °C was kept during electrospinning. Chromatographic standard EPA 8081 Pesticide Standard Mix (200 µg/ml in hexane:toluene 1:1) was supplied by Sigma-Aldrich. SPME commercial fibre - 100 µm PDMS was obtained from Supelco.

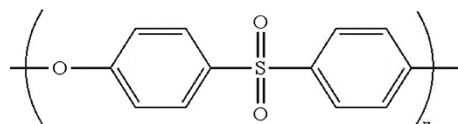


Figure 1 Chemical structure of PES

2. APPARATUS AND EQUIPMENTS

Nanostructure surface of produced polyethersulfone nanofibres on lab-made SPME fibres was documented by SEM microscope (UHR FE-SEM Carl Zeiss ULTRA Plus) (**Figure 2** and **3**). Analytical performance of SPME fibres was tested with gas chromatograph (Thermo Trace 1310) equipped with a mass spectrometer triple quadrupole detector (Thermo TSQ™ 8000 EVO) and a programmed temperature vaporizing injector (PTV). Automatic handling of prepared samples was done by an autosampler (CTC Analytics AG, PAL RTC), which was set to headspace operation mode (samples were agitated during fibre exposure).

A gas chromatography column DB-5MS purchased from Agilent (30 m long, 0.25 µm thick and with 0.25 µm film thickness of stationary phase) was equipped. Temperature program of the chromatographic oven started at 70 °C, graduating by 15 °C per min. to 200 °C, held for 5 minutes, followed by graduating 8 °C per min. to 320 °C, held for 5 minutes. The carrier gas (helium 5.0) flow was adjusted to 2 ml per min. During desorption step, PTV injector was held at 220 °C in splitless mode for 1 minute, for cleaning phase the temperature was set to 250 °C and the flow of carrier gas to 30 ml per min. All of the SPME fibres were tested for different extraction (enrichment) time in the headspace of the measured samples. Enrichment times for all tested fibres were set to 5, 20, 40 and 70 minutes. For each enrichment time were tested 3 different extraction temperature: 50, 70 and 90 °C with same speed of agitator (250 rpm). Temperature of ion source was set to 250 °C and transfer line to 200 °C.

For each tested fibre forty tap water samples spiked with chromatographic standard of organochlorinated pesticides (200 µg·ml⁻¹) were prepared in 20 ml vials capped with PTFE/silicon septa and magnetic cap. Samples were prepared from 10 ml of water and additions of 0.2 µl mixture addition. For salting effect evaluation, 1 or 3 g of sodium chloride were added to selected samples. All measuring was done in duplicates. The retention times of all analytes were determined previously in the fullscan mode of MS detector. Based on this measurement, selected reaction monitoring (SRM) transitions were adjusted to improve detector sensitivity and selectivity for each of chosen analytes.

3. RESULTS AND DISCUSSION

Polyethersulfone nanofibers were successfully prepared (**Figure 2**). The diameter of the prepared nanofibers was in range from 700 to 1400 nm, nevertheless SEM image and high specific surface by BET (32 m²·g⁻¹) document a nanosized pores presence at fibres surface.

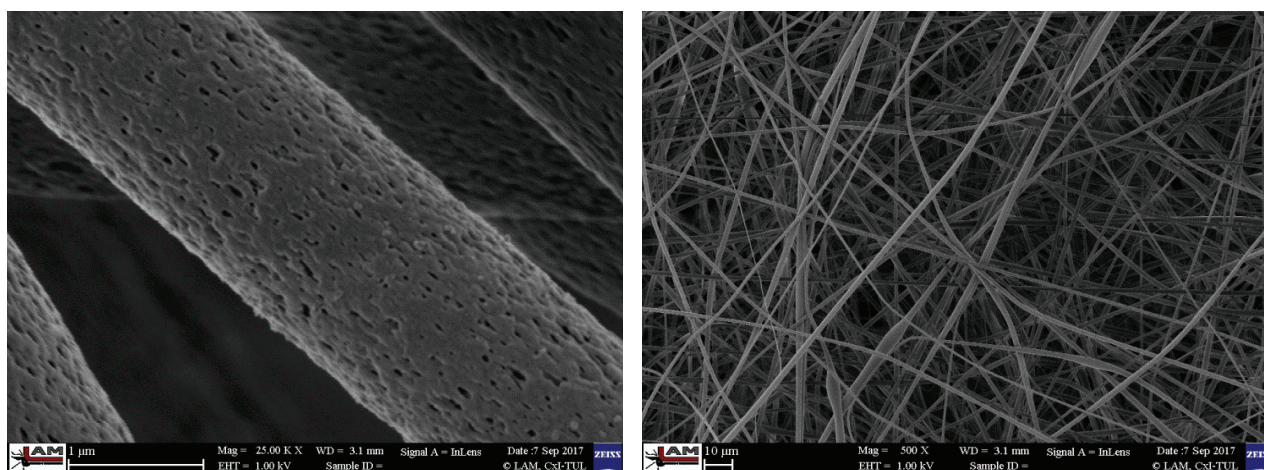
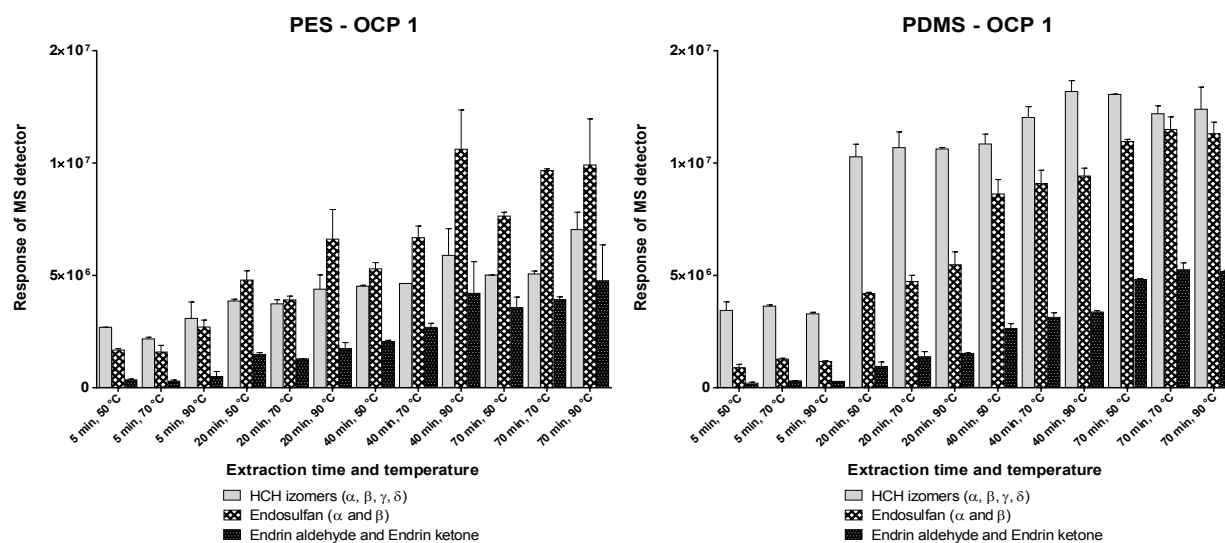
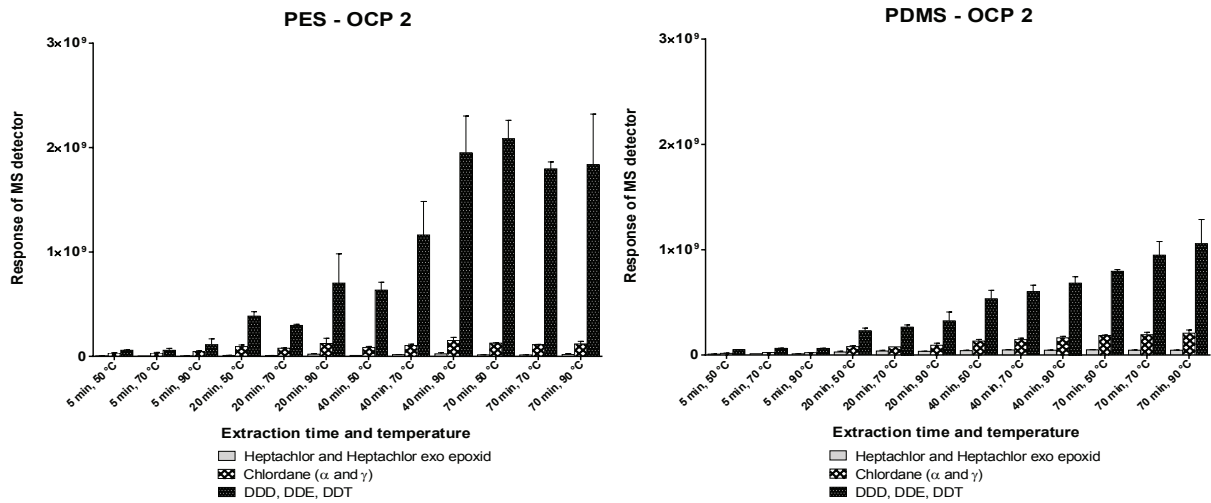


Figure 2 Pictures by SEM microscope (UHR FE-SEM Carl Zeiss ULTRA Plus) of electrospun PES fibres

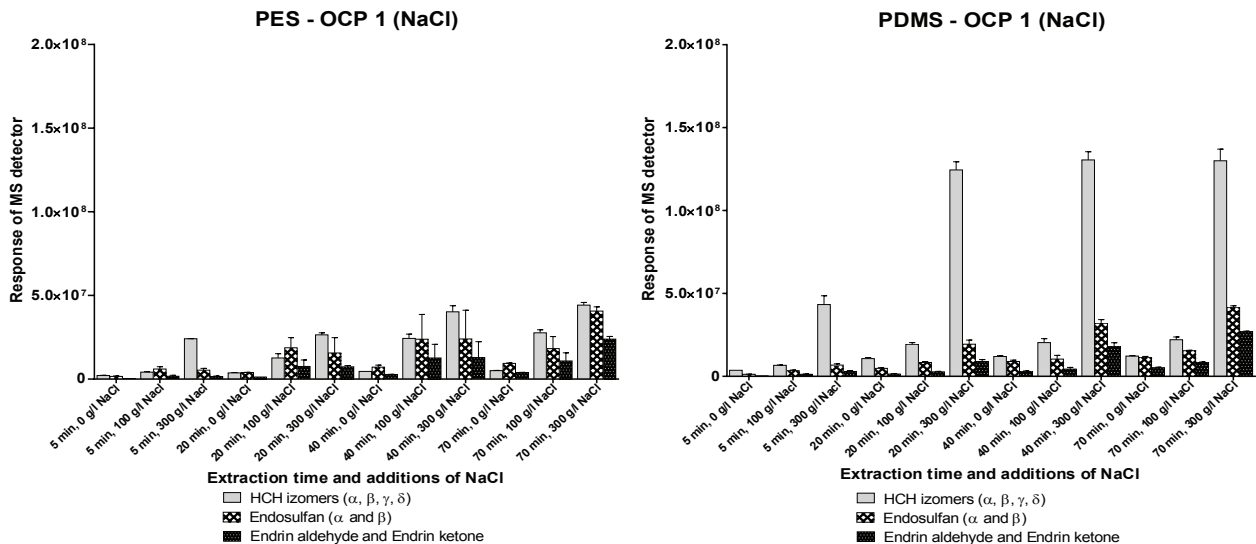
The dependencies of MS detector response peak areas on the different enrichment time, temperature during agitation and additions of sodium chloride are shown in **Figures 3 to 12**. For foresight are obtained data (total measured 20 analytes) grouped together according to the relevance of the analyte.



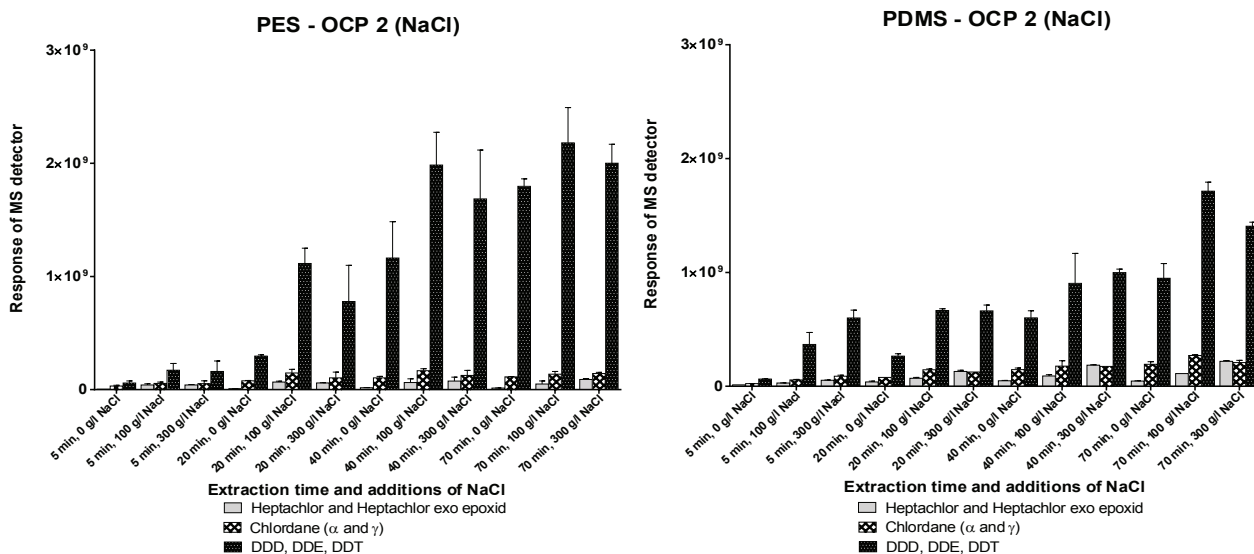


Figures 5 - 6 Comparison of PES and PDMS fibre, GC/MS response after SPME injection (error bars at 1 σ , n = 2)

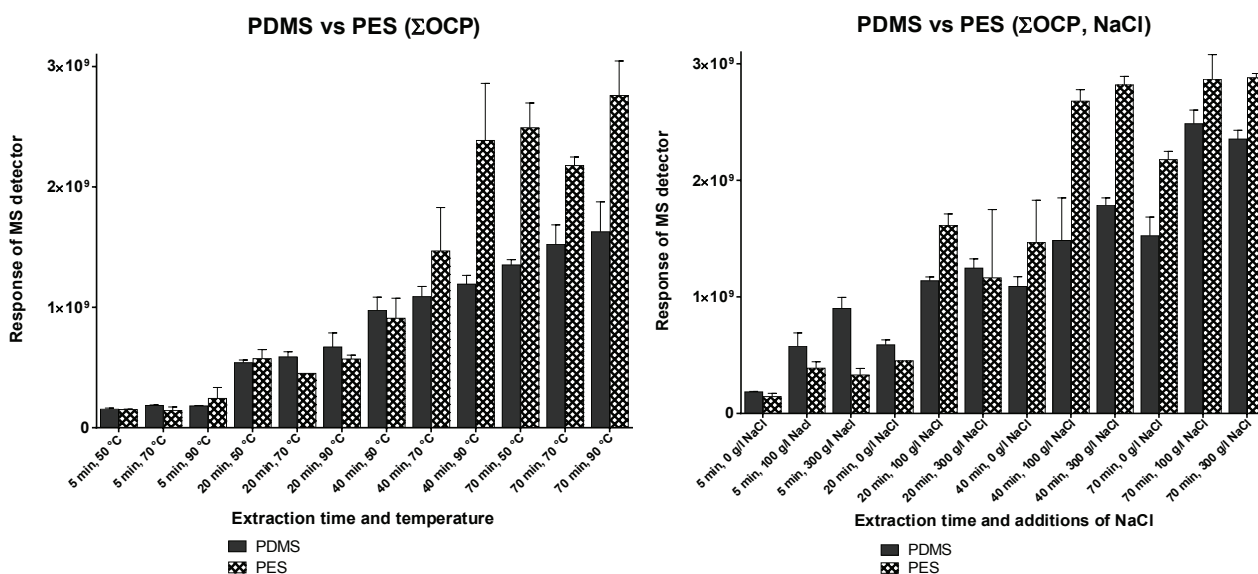
Obtained data indicate that lab-made fibre had higher response especially with longer enrichment time (at least 40 minutes) (**Figure 3 - 6**). It is also apparent, that effect of higher temperature during agitation had little effect on final sorption. Much more effective was the addition of sodium chloride. Even lower concentration showed significantly increase of measured analytes MSMS response. Commercial PDMS fibre had a better performance for HCH isomers when salting out effect was tested (**Figure 7 and 8**).



Figures 7 - 8 Comparison of PES and PDMS SPME fibre, GC/MS response after SPME injection (error bars at 1 σ , n = 2)



Figures 9 - 10 Comparison of PES and PDMS SPME fibre, GC/MS response after SPME injection (error bars at 1σ , $n = 2$)



Figures 11 - 12 Comparison of PES and PDMS SPME fibre, GC/MS response after SPME injection (error bars at 1σ , $n = 2$)

4. CONCLUSION

The polyethersulfone nanofibers were successfully prepared by needle electrospinning. The surface structure analysis by scanning electron microscope (SEM) showed a high porosity surface with the diameter in range from 700 to 1400 nm of the prepared nanofibers. The specific surface at $32\text{ m}^2\cdot\text{g}^{-1}$ was determined. The concept of using polyethersulfone nanofibers as a nanostructured sorbent for analytical purpose has been proved as viable.

The higher temperature of agitation had positive effect on the response of measured analytes. The temperature increase by 20°C resulted in the response increase of 5 to 15 % (sum of OCP). The combination of higher

temperature with longer enrichment time and higher temperature during agitation increased the response of about 50 %. The higher temperature of agitation was more effective during the measurement with PES fibre. This effect was not so strong in case of commercial fibre.

The addition of sodium chloride to the samples had almost always positive effect to the measured response. This effect was most noticeable in case of HCH isomers analysed by PDMS fibre. Similar positive effect appeared during the measurement by lab-made PES fibre.

The parameter of the enrichment time had significantly positive influence on the response of MS detector. For OCP, fibre saturation was not achieved or, in other words, the longer was the time of agitation, the higher the response. In contrast, sorption process seems to reach equilibrium in case at shorted agitation time.

The commercial PDMS fibre had much better performance during measurement of HCH isomers. The biggest differences were observed under high salinity conditions, when the PDMS fibre had almost four times bigger response than the PES fibre. On the other hand, the PES fibre had better response during determination of DDT, DDE and DDD. In this case, the lab-made PES fibre showed of 100 % better response during all tested variables (enrichment time, temperature of agitation and salinity conditions).

In conclusion, a highly porous surface of the prepared PES nanofibers seems to have higher sorption capacity for determination of OCP, than the commonly used thin PDMS polymeric film. However, PES nanofibers show wider data variability than PDMS fibres. Salinity conditions, enrichment time and agitation temperature must be well tuned to optimum values during method development, since they all contribute to the total fibre performance. Further obstacles for fast spreading of nanofibers in analytical chemistry can be seen in the problematic uniformity of nanofiber production (homogeneity) and the nanofibrous SPME possible shorter lifetime.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] PAWLISZYN, J. Handbook of Solid Phase Microextraction, *Chemical Industry Press*, 2009.
- [2] DOONG, R.A. PEI-LIN, L. Determination of organochlorine pesticides and their metabolites in soil samples using headspace solid-phase microextraction. *Journal of Chromatography*, 2001, vol. 918, pp. 177-188.
- [3] YUANYUAN, K. FANG, Z.F. TIANGANG, L. CHENGYONG, S. GANGFENG, O. Preparation of graphene-coated solid-phase microextraction fiber and its application on organochlorine pesticides determination. *Journal of Chromatography*, vol. 1300, pp. 187-192.
- [4] DONG, C. ZENG, Z. LI, X. Determination of organochlorine pesticides and their metabolites in radish after headspace solid-phase microextraction using calix[4]arene fiber. *Talanta*, 2005, vol. 66, no. 3, pp. 721-727.
- [5] LÜ, J. LIU, J. WEI, Y. JIANG, K. FAN, S. LIU, J. JIANG, G. Preparation of single-walled carbon nanotube fiber coating for solid-phase microextraction of organochlorine pesticides in lake water and wastewater. *Journal of Separation Science*, 2007, vol. 30, no. 13, pp. 2138-2143.

- [6] JIE, L. QUANCHAO, Z. YIJIA, Z. QUIANG, W. Polyethersulfone nanofibers for the removal of endocrine disruptors. *Desalination and Water Treatment*, 2011, vol. 29, no. 1-3, pp. 158-163.
- [7] RAHIMPOUR, A. MADAENI, S.S. Improvement of performance and surface properties of nano-porous polyethersulfone (PES) membrane using hydrophilic monomers as additives in the casting solution. *Journal of Membrane Science*, 2010, vol. 360, no. 1-2, pp. 371-379.
- [8] CHANGSHENG, Z. JIMIN, X. FEN, R. SHUNDONG, S. Modification of polyethersulfone membranes - A review of methods. *Progress in Materials Science*, 2013, vol. 58, no. 1, pp. 76-150.