

Electrospun nanofibers as sorbents for the concentration of organic toxicants from aqueous media

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Keywords: sorbents, nanofibers, electrospinning, sorption, organic compounds.

Abstract

The application of new solid phase sorbents on the basis of nanofibres (nonwovens materials) and their composites for the concentration of organic toxicants – the priority pollutants of water bodies is considered. Advantages of electrospun nanofibers are: high specific surface area; highly porous structure; variability of fiber diameter and interfiber distance; improved mechanical properties; the possibility of covalent impregnation of functional groups, etc. Methods for obtaining nanofibres are given by: 1) drawing out long fibers; 2) the template method (nanofilter method); 3) electrospinning. The latter received the largest distribution, which is realized in two versions: capillary and non-capillary. This article is gave a general idea of the potential of using such nanofibers obtained by electrospinning as sorbents of various organic toxicants. Four approaches to obtaining nanofibers for the sorption of various organic analytes have been identified. The first is based on the electrospinning of the solution of the individual polymer. The second is based on the preparation of a solution of a mixture of polymers of various nature, then electrospinning. A third method for obtaining a nanofiber sorbent is to produce a composite based on nanofibers and metal, metal oxides or non-metals nanoparticles. The fourth differs from the first three methods in the step of modifying the surface of the previously obtained nanofiber. The requirements for solvents of the original solid polymers have been determined. Examples of the application of materials obtained by the above methods as sorbents of organic compounds of both hydrophilic and hydrophobic nature from various aqueous media are given. The conditions for the sorption extraction of the compounds to be determined in static and dynamic regimes and certain metrological characteristics (extraction degree, sorption capacity, limit of detection, etc.) are indicated.

References

- [1] Assessment and rationing of the quality of natural waters: criteria, methods, existing problems: a teaching aid. status O.V. Gagarin. *Izhevsk: Udmurt University Publishing House. 2012.* 199p.
- [2] Hygienic standards GN 2.1.5.1315-03 "Maximum Permissible Concentrations (MPC) of Chemicals in the Water of Water-Bodies of Household, Drinking, and Cultural-Household Water Use". Approved Chief State Sanitary Doctor of the Russian Federation of April 27, 2003, No. 78, intro. 15.07.2003. *Moscow: Ministry of Health of the Russian Federation. 1998.* 77p.
- [3] J. Płotka-Wasyłka, N. Szczepańska, M. Guardia, J. Namieśnik. Modern trends in solid phase extraction: new sorbent media. *Trends in Analytical Chemistry. 2015.* Vol.73. P.274-300.
- [4] Nanotechnologies, metrology, standardization and certification in terms and definitions. Ed. M.V. Kovalchuk, P.A. Todua. *Moscow: Technosphere. 2009.* 136p. (russian)
- [5] Terminology and definitions for nanoobjects. Nanoparticle, nanofibre and nanoplate. ISO/TS 27687: 2008.
- [6] A.T. Matveev, I.M. Afanasov. Production of nanofibers by electroforming: a tutorial. *Moscow: Moscow State University Lomonosov. 2010.* P.9-13. (russian)
- [7] L. Persano, A. Camposeo, C. Tekmen, D. Pisignano. Industrial upscaling of electrospinning and applications of polymer nanofibers: a review. *Macromol. Mater. Eng. 298. 2013.* P.504-520.
- [8] S.R.O. Elmarco. Руководство по обслуживанию NS Lab, производственная серия

- [9] H. Bagheri, A. Aghakhani, M. Baghernejad, A. Akbarinejad. Novel polyamide-based nanofibers prepared by electrospinning technique for headspace solid-phase microextraction of phenol and chlorophenols from environmental samples. *Analytica Chimica Acta*. **2012**. Vol.716. P.34-39.
- [10] Q. Xu, S. Wu, M. Wang, X. Yin, Z. Wen, W. Ge, Z. Gu. Electrospun nylon6 nanofibrous membrane as SPE adsorbent for the enrichment and determination of three estrogens in environmental water samples. *Chromatographia*. **2010**. Vol.11. P.487-492.
- [11] H. Bagheri, H. Piri-Moghadam, S. Rastegar. Magnetic and electric field assisted electrospun polyamide nanofibers for on-line μ -solid phase extraction and HPLC. *RSC Adv*. **2014**. Vol.4. P.52590-52597.
- [12] Z. Wei, Q. Zhang, L. Wang, M. Peng, X. Wang, S. long, J. Yang. The preparation and adsorption properties of electrospun aramid nanofibers. *J. of polymer science: part B: polymer physics*. **2012**. Vol.12. P.128-131.
- [13] S. Li, D. Wu, X. Yan, Y. Guan. Acetone-activated polyimide electrospun nanofiber membrane for thin-film microextraction and thermal desorption-gas chromatography-massspectrometric analysis of phenols in environmental water. *J. of Chromatography A*. **2015**. Vol.1411. P.1-8.
- [14] H. Bae, A. Haider, K. Selim, D. Kang, E. Kim, I. Kang. Fabrication of highly porous PMMA electrospun fibers and their application in the removal of phenol and iodine. *J. Polym Res*. **2013**. Vol.20. P.158-164.
- [15] H. Bagheri, A. Akbarinejad, A. Aghakhani. A highly thermal-resistant electrospun-based polyetherimide nanofibers coating for solid-phase microextraction. *Anal. Bioanal. Chem*. **2014**. Vol.406. P.2141-2149.
- [16] Y. Dai, J. Niu, L. Yin, J. Xu, Y. Xi. Sorption of polycyclic aromatic hydrocarbons on electrospun nanofibrous membranes: Sorption kinetics and mechanism. *J. of Hazardous Materials*. **2011**. Vol.192. P.1409-1417.
- [17] J. Niu, J. Xu, Y. Dai, J. Xu, H. Guo, K. Sun, R. Liu. Immobilization of horseradish peroxidase by electrospun fibrous membranes for adsorption and degradation of pentachlorophenol in water. *J. of Hazardous Materials*. **2013**. Vol.246. P.119-125.
- [18] J. Xu, J. Niu, X. Zhang, J. Liu, G. Cao, X. Kong. Sorption of triclosan on electrospun fibrous membranes: Effects of pH and dissolved organic matter. *Emerging Contaminants*. **2015**. Vol.1. P.25-32.
- [19] M. Alnaqbi, Y. Greish, M. Mohsin, E. Elumalai, A. Blooshi. Morphological variations of micro-nanofibrous sorbents prepared by electrospinning and their effects on the sorption of crude oil. *J. of Environmental Chemical Engineering*. **2016**. Vol.4. P.1850-18661.
- [20] R. Chen, Y. Yang, N. Wang, L. Hao, L. Li, X. Guo, J. Zhang, Y. Hu, W. Shen. Application of packed porous nanofibers – Solid-phase extraction for the detection of sulfonamide residues from environmental water samples by ultra high performance liquid chromatography with mass spectrometry. *J. of Separation Science*. **2014**. Vol.24. P.534-539.
- [21] S. Haidera, F. Binagaga, A. Haiderb, A. Mahmooda, N. Shahc, W. Al-Masrya, S. Khand, S. Ramaya. Adsorption kinetic and isotherm of methylene blue, safranin T and rhodamine B onto electrospun ethylenediamine-grafted-polyacrylonitrile nanofibers membrane. *Desalination and Water Treatment*. **2015**. Vol.55. P.1609-1619.
- [22] J. Lin, B. Ding, J. Yang, J. Yu, G. Sun. Subtle regulation of the micro- and nanostructures of electrospun polystyrene fibers and their application in oil absorption. *Nanoscale*. **2012**. Vol.4. P.176-182.
- [23] J. Lin, Y. Shang, B. Ding, J. Yang, J. Yu, S. Al-Deyab. Nanoporous polystyrene fibers for oil spill cleanup. *Marine Pollution Bulletin*. **2012**. Vol.64. P.347-352.
- [24] J. Wu, N. Wang, L. Wang, H. Dong, Y. Zhao, L. Jiang. Electrospun Porous Structure Fibrous Film with High Oil Adsorption Capacity. *ACS Appl. Mater. Interfaces*. **2012**. Vol.4. P.3207-3212.
- [25] H. Bagheri, H. Najarzadekan, A. Roostaie. Electrospun polyamide–polyethylene glycol nanofibers for headspace solid-phase microextraction. *J. Sep. Sci*. **2014**. Vol.37. P.1880-1886.
- [26] H. Bagheri, A. Aghakhani. Polyaniline-nylon-6 electrospun nanofibers for headspace adsorptive microextraction. *Analytica Chimica Acta*. **2012**. Vol.713. P.63-69.
- [27] H. Bagheri, A. Aghakhani, M. Akbari, Z. Ayazi. Electrospun composite of polypyrrole-polyamide as a micro-solid phase extraction sorbent. *Anal. Bioanal. Chem*. **2011**. Vol.400. P.3607-3613.
- [28] H. Bagheri, Z. Ayazi, A. Aghakhani, N. Alipour. Polypyrrole/polyamide electrospun-based sorbent for microextraction in packed syringe of organophosphorous pesticides from aquatic samples. *J. Sep. Sci*. **2012**. Vol.35. P.114-120.
- [29] F. Qi, X. Li, B. Yang, F. Rong, Q. Xu. Disks solid phase extraction based polypyrrole functionalized core–shell nanofibers mat. *Talanta*. **2015**. Vol.144. P.129-135.
- [30] Q. Zhou, R. Xu. Adsorption of 2,4-dichlorophenol on Meta-Aramid/Poly (acrylic Acid) composite nanofibrous membranes. *Advanced Materials Research Vols*. **2013**. Vol.610-613. P.551-555.

- [31] J. Xu, J. Niu, S. Zhang. Sorption of perfluorooctane sulfonate (PFOS) on electrospun fiber membranes. *Procedia Environmental Sciences*. **2013**. Vol.18. P.472-477.
- [32] L. Peng, Q. Ying, Z. Lili, Y. Dahu, S. Haixiang, H. Yingfei, L. Shuo, L. Qi. Electrospun PS/PAN fibers with improved mechanical property for removal of oil from water. *Marine Pollution Bulletin*. **2015**. Vol.93. P.75-80.
- [33] D. Qi, X. Kang, L. Chen, Y. Zhang, H. Wei, Z. Gu. Electrospun polymer nanofibers as a solid-phase extraction sorbent for the determination of trace pollutants in environmental water. *Anal Bioanal Chem*. **2008**. Vol.390. P.929-938.
- [34] H. Bahgeri, O. Rezvani, S. Banihashemi. Core-shell electrospun polybutylene terephthalate/polypyrrole hollow nanofibers for micro-solid phase extraction. *J. Chromatogr. A*. **2016**. Vol.1434. P.19-28.
- [35] F. Song, X. Wang, Y. Wang. Poly (N-isopropylacrylamide)/poly (ethylene oxide) blend nanofibrous scaffolds: Thermo-responsive carrier for controlled drug release. *Colloids and Surfaces B: Biointerfaces*. **2011**. Vol.88. P.749-754.
- [36] S. Dadvar, H. Tavanai, M. Morshed, M. Ghiaci. A study on the kinetics of 2-chloroethyl ethyl sulfide adsorption onto nanocomposite activated carbon nanofibers containing metal oxide nanoparticles. *Separation and Purification Technology*. **2013**. Vol.114. P.24-30.
- [37] H. Bagheri, A. Roostaie. Roles of inorganic oxide nanoparticles on extraction efficiency of electrospun polyethylene terephthalate nanocomposite as an unbreakable fiber coating. *J. Chromatogr. A*. **2015**. Vol.1375. P.8-16.
- [38] X. He, G. Zhu, J. Yin, Q. Zhao, B. Yuan, Y. Feng. Electrospun polystyrene/ oxidized carbon nanotubes film as both sorbent for thin film microextraction and matrix for matrix assisted laser desorption/ionization time-of-flight mass spectrometry. *J. Chromatogr. A*. **2014**. Vol.1351. P.29-36.
- [39] K. Yoshimatsu, L. Ye, J. Lindberg, I. Chronakis. Selective molecular adsorption using electrospun nanofiber affinity membranes. *Biosensors and Bioelectronics*. **2008**. Vol.23. P.1208-1215.
- [40] M. Teng, F. Li, B. Zhang, A. Taha. Electrospun cyclodextrin-functionalized mesoporous polyvinyl alcohol/SiO₂ nanofiber membranes as a highly efficient adsorbent for indigo carmine dye. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. **2011**. Vol.385. P.229-234.
- [41] L. Zhang, Y. Guo, W. Chi, H. Shi, H. Ren, T. Guo. Electrospun Nanofibers Containing p-Nitrophenol Imprinted Nanoparticles for the Hydrolysis of Paraoxon. *Chinese Journal of Polymer Science*. **2014**. Vol.32. P.146-1478.
- [42] M. Aassar, M. Kady, H. Hassan, S. Deyab. Synthesis and characterization of surface modified electrospun poly(acrylonitrile-co-styrene)nanofibers for dye decolorization. *J. of the Taiwan Institute of Chemical Engineers*. **2015**. P.1-9.
- [43] S. Haidera, F. Binagaga, A. Haiderb, A. Mahmooda, N. Shahc, W. Al-Masrya, S. Khand, S. Ramay. Adsorption kinetic and isotherm of methylene blue, safranin T and rhodamine B onto electrospun ethylenediamine-grafted-polyacrylonitrile nanofibers membrane. *Desalination and Water Treatment*. **2014**. Vol.11. P.210-221.
- [44] L. Qian, X. Li, F. Qi, J. Li, L. Lu, Q. Xu. An amino-functionalized grooved nanofiber mat for solid-phase extraction of phenolic pollutants. *Microchimica Acta*. **2017**. Vol.184. P.2861-2870.
- [45] A. Almasiana, Gh. Chizari Fardb, M. Parvinzadeh Gashtic, M. Mirjalilic, Z. Mokhtari Shourijehd. Surface modification of electrospun PAN nanofibers by amine compounds for adsorption of anionic dyes. *Desalination and Water Treatment*. **2015**. Vol.15. P.412-427.
- [46] M. Min, L. Shen, G. Hong, M. Zhu, Y. Zhang, X. Wang, Y. Chen, B. Hsiao. Micro-nano structure poly(ether sulfones)/poly(ethyleneimine) nanofibrous affinity membranes for adsorption of anionic dyes and heavy metal ions in aqueous solution. *Chemical Engineering Journal*. **2012**. Vol.197. P.88-100.
- [47] J. Yan, Y. Huang, Y. Miao, W. Tjiu, T. Liu. Poly dopamine-coated electrospun poly(vinyl alcohol)/poly(acrylic acid) membranes as efficient dye adsorbent with good recyclability. *J. of Hazardous Materials*. **2015**. Vol.283. P.730-73.