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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Electrospun Polystyrene Nanofiber as an Adsorbent for Solid-Phase Extraction of Disulfine Blue from Aqueous Samples

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Abstract In this research, polystyrene nanofibers were synthesized by electrospinning method and used as adsorbent in solid-phase extraction of Disulfine blue from aqueous solutions. Some important parameters affecting extraction efficiency including sample flow rate through the adsorbent, ionic strength, pH of the sample solution, weight of adsorbent, volume, and type of eluent were evaluated and optimized. Under the optimized conditions, the calibration graph was linear in the range of 6.4–1000 $\mu g\,L^{-1}$ with correlation coefficient (r^2) of 0.9962. The limit of detection and enhancement factor of proposed method, for extraction from 50 mL sample solution, were obtained as 2 $\mu g\,L^{-1}$ and 9.5, respectively. Finally, the proposed method was successfully applied for extraction and measurement of Disulfine blue from real samples, and satisfactory results were obtained.

Keywords Nanofibers · Electrospinning · Solid-phase extraction · Disulfine blue

1 Introduction

Nanofibers generally are considered as fibers with diameters less than 1 μm [1]. Nanofibers have several characteristics such as very high surface-to-volume ratio, superior mechanical performance, and tunable porosity. These prominent properties make them as a good option for many significant applications [2]. There are several methods for producing fibers. The most of them that generate polymeric fibers in nanoscale are drawing [3], template synthesis [4], phase separation [5], self-assembly [6], and electrospinning [7,8]. Among these, electrospinning is a simple and inexpensive technique and can be used for a wide range of polymer and copolymer materials by using high electrostatic forces [9,10]. Furthermore, the morphology and diameter of electrospun fibers can be easily controlled in a wide range (several nanometers to several micrometers) by spinning conditions such as solution parameters (concentration and molecular weight of polymer, viscosity, conductivity, and surface tension of solution), process parameters (applied electric field, feed rate, and tip to collector distance), and ambient parameters (the humidity and temperature during the process) [11–13]. Electrospun nanofiber membranes can be used as sorbent for extraction and preconcentration methods due to their larger specific surface area and flexibility in surface functionalities [14].

Solid-phase extraction (SPE) is one of the useful sample preparation methods that are used for cleanup, extraction, and preconcentration of target analytes from aqueous samples. It is an attractive method that reduces extraction time, disposal costs, and solvent consumption [15,16]. The type and properties of the adsorbent materials are the most important part of SPE procedure because they have direct influence on the sample selectivity and adsorption capacity [17]. SPE can be used for extraction and preconcentration of different types of metal ions [18,19], various organic compounds [20], pharmaceutical compounds [21], and environmental pollutants [22]. Some researchers successfully used electrospun polystyrene nanofibers for extraction and removal of pollutants from real samples [22–25].

Dyes are the most important water pollutants and often are resistant against physical, chemical, and biological treatment processes [26]. Disulfine blue (VN 150) is a hazardous dye that is widely used for dyeing of wool and silk, carbon paper, cosmetics, and leather [27,28]. It shows several side

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effects such as eye and skin sensitivity. Also, inhalation of its dust may cause digestion and respiratory tract irritation. So, extraction and preconcentration of Disulfine blue is required for its determination in low concentration levels or in polluted water samples where the direct photometric measurement is not possible.

In this work, polystyrene nanofibers (PS NFs) were produced via electrospinning method, and the morphology and diameter of NFs were studied by SEM technique. Then, their capability as adsorbent in SPE for extraction of Disulfine blue from aqueous solutions was investigated. In order to achieve higher extraction efficiency, the experimental parameters affecting the extraction performance were investigated and optimized using univariate method.

2 Experimental

2.1 Chemicals and Materials

All materials used in this study, including dimethyl formamide (DMF), tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH), sodium chloride, hydrochloric acid (37 % w/w), sodium hydroxide, and Disulfine blue (Acid Blue, 1 Hydrogen [4-[4-(diethylamino)-2′,4′-disulfonatobenzhydry lidene]cyclohexa-2,5-dien-1-ylidene] diethyl ammonium, sodium salt), were purchased with high purity from Merck (Darmstadt, Germany), Sigma-Aldrich (Milwaukee, WI, USA), and Merck Millipore companies. PS granules were purchased from Tabriz Petrochemical with industrial code of GPPS 1460, melt flow index (200 °C–5 kg): 6.5 g/10 min, and density: 1.04 kg L^{-1} (Tabriz, Iran). All stock and working solutions were prepared using double distilled water.

Standard stock solution of Disulfine blue (Fig. 1) was prepared in double distilled water with a concentration of 100 mg L^{-1} and stored in a refrigerator at 4 °C. Required concentrations of Disulfine blue were prepared by diluting the stock standard solution with double distilled water.

2.2 Instruments

The syringe pump and high-voltage power supply were purchased from Fanavaran Nano-Meghyas Company (Tehran, Iran). For protection against high voltage, electrospinning process was carried out in a handmade box (90 × 50 × 60 cm). The UV–Vis spectrophotometer from Mapada Company (6300PC, China) was applied for spectrophotometric measurement of Disulfine blue. SEM images were obtained with a Seron Technology AIS2100 SEM instruments. The handmade glass cartridge was made with a glass tube length of 10 cm and inner diameter of 1 cm. The vacuum pump was used from Sparmax (TC2000 MV, Taiwan), and the pH of solutions was measured using EDT pH meter (GP 353, England).

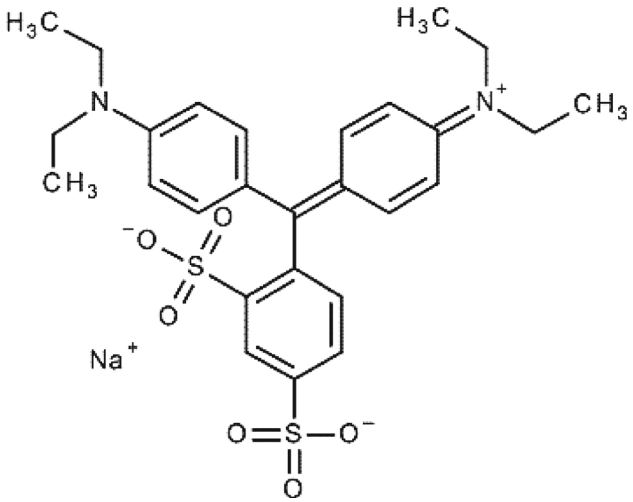

Fig. 1 Chemical structure of Disulfine blue

2.3 Electrospinning Synthesis of Nanofibers

For the electrospinning synthesis of PS NFs, firstly some of the experimental factors affecting the conversion of polymeric solution into NFs including PS concentration in solution, inner diameter of the needle, polymeric solution feed rate, magnitude of applied voltage, and distance of needle tip to collector were investigated and optimized (PS concentration: 15 % w/v, syringe inner diameter: 0.4 mm, feed rate: 0.1 mL h^{-1}, distance to collector: 15 cm, voltage: 20 kV). For synthesis of PS NFs, PS solution (15 % w/v) was prepared in a mixture of DMF:THF (8:2, v/v), and the solution was stirred for 5 h at room temperature. This solution was loaded into a 10 mL polyethylene syringe (inner diameter: 0.4 mm) equipped with a flat steel syringe needle and placed into a syringe pump. The feed rate of precursor polymeric solution from syringe was set at 0.1 mL h^{-1} on the syringe pump. The distance between the needle tip and the aluminum collector plate was adjusted as 15 cm. The anode was connected to needle, a grounded electrode to the collector, and a high voltage of 20 kV was applied between the needle and the collector. Finally, PS NFs were produced on the aluminum collector. A schematic diagram of electrospinning method is shown in Fig. 2.

2.4 Electrospun PS NFs as Adsorbent for Solid-Phase Extraction

A certain weight of synthesized PS NFs was used as adsorbent in SPE method. For this purpose, electrospun PS NFs were packed compactly into a 10 cm handmade glass cartridge between two pieces of cotton to retain the PS NFs in the cartridge. The cartridge was connected to a vacuum pump using a vacuum Erlenmeyer. The PS NFs were preconditioned with passing 2 mL of MeOH and 4 mL of double

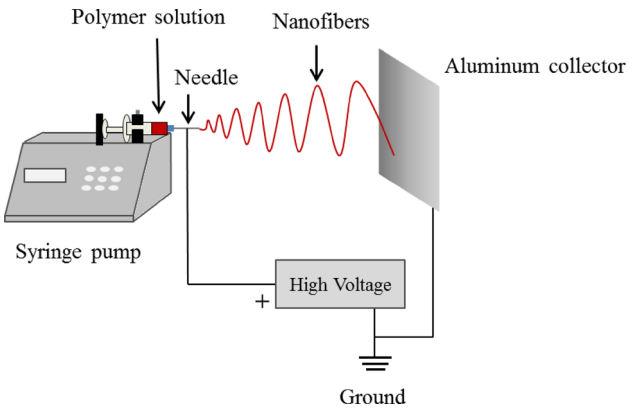

Fig. 2 A schematic diagram of the electrospinning method

distilled water to clean it from possible interferences and to achieve maximum extraction efficiency. Then, 50 mL of aqueous sample of Disulfine blue (1 mg L^{-1}) was loaded through the cartridge at different flow rates. At this step, analyte was adsorbed on the surface of adsorbent and changed its color from white to blue. After that, elution step was done by 3 mL of MeOH to desorb dye from the surface of PS NFs, and the eluted dye was determined by UV–Vis spectroscopy at $\lambda_{max} = 638$ nm.

3 Results and Discussion

Disulfine blue can be adsorbed and extracted on the surface of packed PS NFs via π–π interactions between the aromatic groups in Disulfine blue and benzene rings in polymer structure. To achieve the best performance of adsorption, various experimental parameters affecting the electrospinning and SPE procedures were investigated and optimized.

3.1 Optimization of Electrospinning Condition for Preparation of PS NFs

In order to optimize the electrospinning conditions, the concentration of PS solutions (15–25 % w/v), inner diameters of the needle (0.4 and 0.3 mm), the sample flow rate (0.1–0.5 mL h^{-1}), the applied voltage (15–20 kV), and the distances between the needle and collector (15–20 cm) were studied and optimized. According to the results, optimized electrospinning conditions were obtained as 15 % w/v PS concentration, 0.4 mm needle diameter, 0.1 mL h^{-1} sample flow, 20 kV voltage, and 15 cm distance between the needle and collector. At the optimum conditions of electrospinning process, the product formation rate was 15 mg h^{-1}. Morphology of synthesized PS NFs was studied using a scanning electron microscope (SEM). As shown in Fig. 3, the diameter of NFs was obtained between 380 and 500 nm.

3.2 Effect of Sample Flow Rate, Ionic Strength, and pH on the SPE by Electrospun PS NFs

In the SPE, the sample flow rate through the NF adsorbent is one of the critical parameters affecting the extraction efficiency. The flow rate of dye sample solution was studied with a controllable tap of the cartridge and a vacuum pump in the range of 0.5–25 mL min^{-1} (extraction conditions: 50 mL of 5 mg L^{-1} of Disulfine blue, pH 5.6, 0.015 g PS NFs, eluting solvent: 3 mL MeOH). According to the results, for the lower sample flow rates (0.5–5 mL min^{-1}), the extraction efficiency was better than higher flow rates by a factor of 1.2 times due to more contact times of sample with adsorbent. Therefore, for reduction in extraction time, 2.5 mL min^{-1} was selected as optimum sample flow rate for further studies.

The presence of ionic species in sample decreases the solubility of polar analytes in aqueous phase due to salting out effect [29]. In this study, the effect of ionic strength of the sample solution was examined with addition of sodium chloride into the dye solution in the range of 0–15 % w/v. According to the results, the best extraction efficiency was achieved with addition of 2 % w/v sodium chloride salt (extraction conditions: 50 mL of 1 mg L^{-1} of Disulfine blue, pH 5.6, 0.015 g PS NFs, sample flow rate: 2.5 mL min^{-1}, eluting solvent: 3 mL MeOH).

For the assessment of the effect of solution pH on the extraction efficiency, the pH of the dye sample (1 mg L^{-1}) was investigated in the pH range of 3–9. According to the

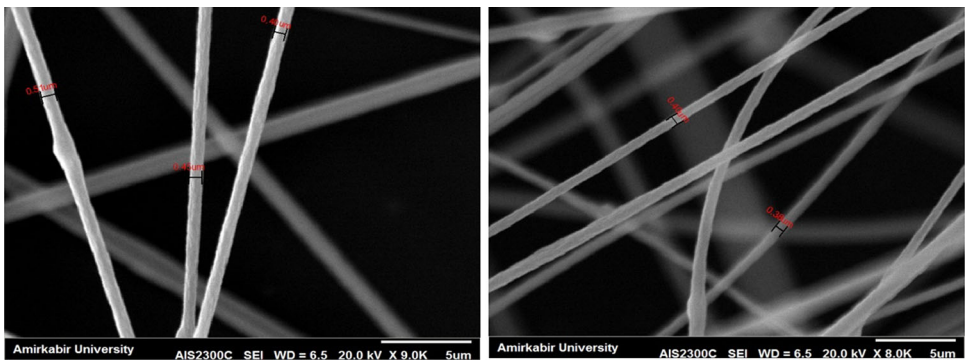

Fig. 3 SEM images of polystyrene nanofibers

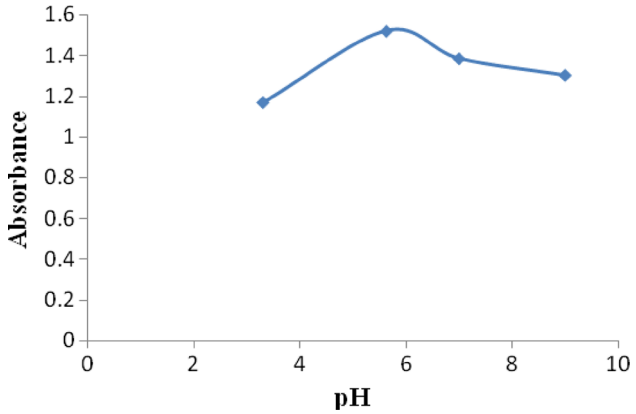

Fig. 4 Effect of pH on the extraction efficiency (extraction conditions: 50 mL of 1 mg L^{-1} of Disulfine blue, salt addition: 2 % w/v of NaCl, 0.015 g PS nanofibers, sample flow rate: 2.5 mL min^{-1}, eluent solvent: 3 mL MeOH)

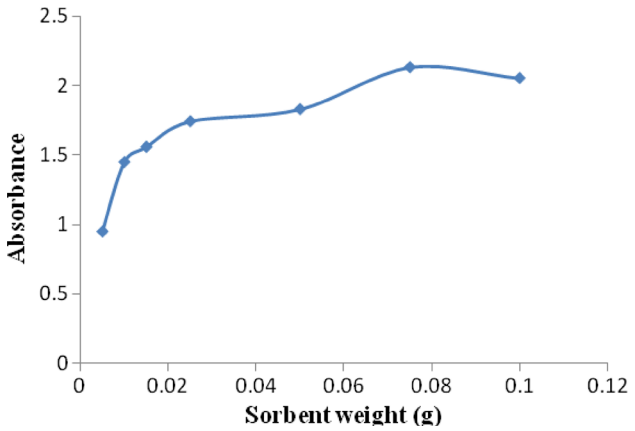

Fig. 5 Effect of sorbent weight on the extraction efficiency (extraction conditions: 50 mL of 1 mg L^{-1} of Disulfine blue, pH 5.6, salt addition: 2 % w/v of NaCl, sample flow rate: 2.5 mL min^{-1}, eluent solvent: 3 mL MeOH)

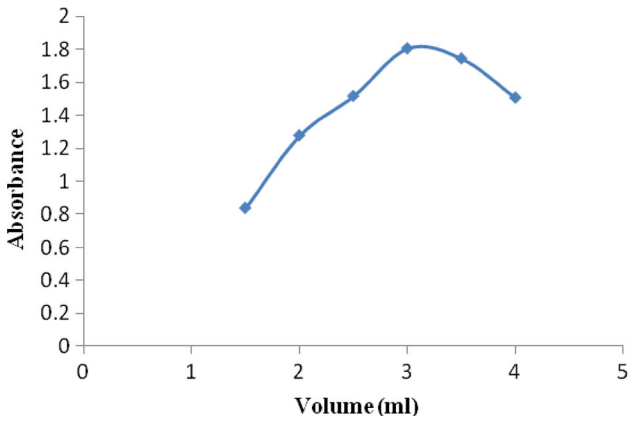

Fig. 6 Effect of eluent volume on the extraction efficiency (extraction conditions: 50 mL of 1 mg L^{-1} of Disulfine blue, pH 5.6, salt addition: 2 % w/v of NaCl, sample flow rate: 2.5 mL min^{-1})

results of Fig. 4, the best extraction efficiency was achieved at pH 5.6.

At lower pHs, the sulfonate groups are protonated, and the positive Disulfine blue cannot be adsorbed effectively on the NFs surface. Also, at higher pHs, the net charge of dye was negative, and it can repelled by the NFs that have negative charge due to adsorption of hydroxyl groups. Therefore, pH 5.6 was selected as optimum pH for further experiments.

3.3 Effect of PS NF Weight on the SPE of Disulfine Blue

The effect of adsorbent weight on the extraction efficiency was studied in the range of 0.005–0.1 g of PS NFs, and the results are shown in Fig. 5. With the increase in adsorbent weight, more interaction was occurred between analyte and adsorbent, and adsorption capacity of NFs increased. Using cartridge containing greater adsorbent mass, more volume of eluent solvent is required, which reduces the method sensitivity. Considering to the results and cost-effectiveness of synthesized NFs, 0.05 g of PS NFs was selected as the optimum weight for further studies.

3.4 Effect of Eluent Type and Volume

In order to desorb the Disulfine blue from the NFs, a proper eluent solvent should be used to overcome the π–π interactions between the aromatic groups in Disulfine blue and benzene rings in NFs structure. For this purpose, MeOH volumes in the range of 1.5–4 mL were passed through the cartridge. As illustrated in Fig. 6, the highest preconcentration was achieved at 3 mL of MeOH.

Lower volumes were not enough for completely desorption of Disulfine blue from NFs. On the other hand, with increasing the eluent volume to more than 3 mL, preconcentration factor was reduced due to dilution of eluent phase.

To investigate the eluent type, 3 mL of MeOH, EtOH, and double distilled water was passed through the cartridge. The results showed the elution order of MeOH $\geq$ EtOH $\gg$ double distilled water for Disulfine blue desorption. Finally, MeOH (3 mL) was used as eluent for further studies.

3.5 Analytical Figures of Merit

The linear dynamic range (LDR), limit of detection (LOD), limit of quantitation (LOQ), and enhancement factor (EF) of the suggested method were investigated under optimized conditions (1 mg L^{-1} of Disulfine blue, pH 5.6, salt addition: 2 % w/v of NaCl, sample flow rate: 2.5 mL min^{-1}, and sample volume: 50 mL). The calibration curves were obtained without and after preconcentration of Disulfine blue. The LDR of direct measurement without preconcentration was observed in the range of 50–5000 µg L^{-1} with correlation coefficient (r^2) of 0.99997, and the LDR after preconcentration was

Table 1 Analytical results for determination of Disulfine blue in real samples under the optimized conditions

Sample	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	Relative recovery (%)	RSD[b] (%) ($n = 4$)
Tap water	50.0	54.2 ± 0.0018	108.5	2.9
Well water	50.0	53.0 ± 0.0016	106.0	2.6
River water	50.0	51.1 ± 0.0012	102.2	2.2

[a] Mean of four replicate ± standard deviation
[b] Relative standard deviation

achieved in the range of 6.4–1000 $\mu g L^{-1}$ with r^2 of 0.9962. The LOD and LOQ of proposed method were calculated from $C_{LOD} = 3S_b/m$ and $C_{LOQ} = 10S_b/m$ that S_b is the standard deviation of five replicate blank preconcentration, and m is the slope of calibration graph after preconcentration [30]. The LOD and LOQ of the proposed method were calculated as 2 and 6.4 $\mu g\ L^{-1}$ under optimized conditions. The EF of the proposed method (as the ratio of the slope of calibration curve after preconcentration to that without preconcentration) was calculated as 9.5.

3.6 Analysis of Real Samples

To evaluate the applicability of the proposed SPE method for extraction of Disulfine blue from real samples, three real samples (tap, well, and river water samples) were investigated. Firstly, all of the samples were extracted using proposed method, and the results showed the absence of Disulfine blue in samples. Secondly, in order to study the matrix effects, the samples were spiked with 50 $\mu g L^{-1}$ of Disulfine blue. The accuracy and precision of the method were examined by extracting from 50 mL of each real sample under the optimum conditions and expressed as relative recovery and relative standard deviation percent (RSD %). As shown in Table 1, the relative recoveries for SPE of Disulfine blue were varied in the range of 102–108 % and the RSD % were between 2.2 and 2.9 %.

4 Conclusion

Electrospun nanofibers have large surface area and good mechanical properties that can be suitable for extraction of analytes by adsorption based on chemical or physical interactions. The results show that using PS NFs as adsorbent in SPE is an effective method for extraction and preconcentration of Disulfine blue in different water samples. The recovery data of proposed method for real samples showed the applicability of the method for different aqueous samples.

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References

1. Hasan, M.M.; Nayem, K.A.; Hossain, M.B.; Nahar, S.: Production of tissue engineering scaffolds from poly caprolactone (PCL) and its microscopic analysis. Int. J. Text. Sci. **3**, 39–43 (2014)
2. Huang, Z.M.; Zhang, Z.Y.; Kotaki, M.; Ramakrishna, S.: A review on polymer nanofibers by electrospinning andtheir applications in nanocomposites. Compos. Sci. Technol. **63**, 2223–2253 (2003)
3. Ondarçuhu, T.; Joachim, C.: Drawing a single nanofibre over hundreds of microns. Europhys. Lett. **42**, 215–220 (1998)
4. Feng, L.; Li, S.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D.: Super-hydrophobic surface of aligned polyacrylonitrile nanofibers. Angew. Chem. Int. Edit. **41**, 1221–1223 (2002)
5. Ma, P.X.; Zhang, R.: Synthetic nano-scale fibrous extracellular matrix. J. Biomed. Mater. Res. **46**, 60–72 (1999)
6. Whitesides, M.G.; Grzybowski, B.: Self-assembly at all scales. Science **295**, 2418–2421 (2002)
7. Deitzel, J.M.; Kleinmeyer, J.D.; Hirvonen, J.K.; Beck Tan, N.C.: Controlled deposition of electrospun poly(ethylene oxide) fibers. Polymer **42**, 8163–8170 (2001)
8. Baji, A.; Mai, Y.W.; Wong, S.C.; Abtahi, M.: Electrospinning of polymer nanofibers: effects on oriented morphology, structures and tensile properties. Compos. Sci. Technol. **70**, 703–718 (2010)
9. Newsome, T.; Zewe, J.; Olesik, S.: Electrospun nanofibrous solid-phase microextraction coatings for preconcentration of pharmaceuticals prior to liquid chromatographic separations. J. Chromatogr. A **1262**, 1–7 (2012)
10. Beachley, V.; Wen, X.: Polymer nanofibrous structures: fabrication, biofunctionalization, and cell interactions. Prog. Polym. Sci. **35**, 868–892 (2010)
11. Beak, D.H.; Ki, C.S.; Um, I.C.; Park, Y.H.: Metal ion adsorbability of electrospun wool keratose/silk fibroin blend nanofiber mats. Fibers Polym. **8**, 271–277 (2007)
12. Rodoplu, D.; Mutlu, M.: Effects of electrospinning setup and process parameters on nanofiber morphology intended for the modification of quartz crystal microbalance surfaces. J. Eng. Fiber. Fabr. **7**, 118–123 (2012)
13. Bhardwaj, N.; Kundu, S.C.: Electrospinning: a fascinating fiber fabrication technique. Biotechnol. Adv. **28**, 325–347 (2010)
14. Bagheri, H.; Akbarinejad, A.; Aghakhani, A.: A highly thermal-resistant electrospun-based polyetherimide nanofibers coating for solid-phase microextraction. Anal. Bioanal. Chem. **406**, 2141–2149 (2013)
15. Moors, M.; Massart, D.L.; McDowall, R.D.: Analyte isolation by solid-phase extraction (SPE) on silica-bonded phases-classification and recommended practices. Pure Appl. Chem. **66**, 277–304 (1994)
16. Anbia, M.; Ghasemian, M.B.; Shariati, S.; Zolfaghari, G.: Employing a new modified nanoporous carbon for extraction and determination of 1,10-phenanthroline and 2,20-bipyridine by SPE and use of the Taguchi optimization method. Anal. Methods **4**, 4220–4229 (2012)
17. Chigome, S.; Torto, N.: Electrospun nanofiber based solid phase extraction. Trends Anal. Chem. **38**, 21–31 (2012)
18. Alqadami, A.A.; Abdalla, M.A.; AlOthman, Z.A.; Omer, K.: Application of solid phase extraction on multi walled carbon nanotubes of some heavy metal ions to analysis of skin whitening cosmetics using ICP-AES. Int. J. Environ. Res. Public Health **10**, 361–374 (2013)
19. Shariati, S.; Yamini, Y.; Faraji, M.; Saleh, A.: On-line solid phase extraction coupled to ICP-OES for simultaneous preconcentra-

tion and determination of some transition elements. Microchim. Acta **165**, 65–72 (2009)
20. Shi, L.; Liu, X.; Li, H.; Niu, W.; Xu, G.: Application of ceramic carbon materials for solid-phase extraction of organic compounds. Anal. Chem. **78**, 1345–1348 (2006)
21. Zhang, Z.L.; Zhou, J.L.: Simultaneous determination of various pharmaceutical compounds in water by solid-phase extraction–liquid chromatography–tandem mass spectrometry. J. Chromatogr. A **1154**, 205–213 (2007)
22. Qi, D.; Kang, X.; Chen, L.; Zhang, Y.; Wei, H.; Gu, Z.: Electrospun polymer nanofibers as a solid-phase extraction sorbent for the determination of trace pollutants in environmental water. Anal. Bioanal. Chem. **390**, 929–938 (2007)
23. Shin, C.; Chase, G.G.; Reneker, D.H.: Recycled expanded polystyrene nanofibers applied in filter media. Colloids Surf. A **262**(1–3), 211–215 (2005)
24. Chigome, S.; Darko, G.; Buttner, U.; Torto, N.: Semi-micro solid phase extraction with electrospun polystyrene fiber disks. Anal. Methods **2**, 623–626 (2010)
25. Kang, X.; Pan, C.; Xu, Q.; Yao, Y.; Wang, Y.; Qi, D.; Gu, Z.: The investigation of electrospun polymer nanofibers as a solid-phase extraction sorbent for the determination of trazodone in human plasma. Anal. Chim. Acta **587**, 75–81 (2007)
26. Yang, W.; Wu, D.; Fu, R.: Effect of surface chemistry on the adsorption of basic dyeson carbon aerogels. Colloids Surf. A **312**, 118–124 (2008)
27. Ahmad, R.; Kumar, R.: Comparative adsorption study for the removal of Alizarin Red S and patent Blue VF by using mentha waste. Curr. World Environ. **3**, 261–268 (2008)
28. Scherer, K.; Bircher, A.J.; Figueiredo, V.: Blue dyes in medicine—a confusing terminology. Contact Dermat. **54**, 231–232 (2006)
29. Eisert, R.; Pawliszyn, J.: New trends in solid-phase microextraction. Crit. Rev. Anal. Chem. **27**, 103–135 (1997)
30. Faraji, M.; Yamini, Y.; Shariati, S.: Application of cotton as a solid phase extraction sorbent for on-line preconcentration of copper in water samples prior to inductively coupled plasma optical emission spectrometry determination. J. Hazard. Mater. **166**, 1383–1388 (2009)