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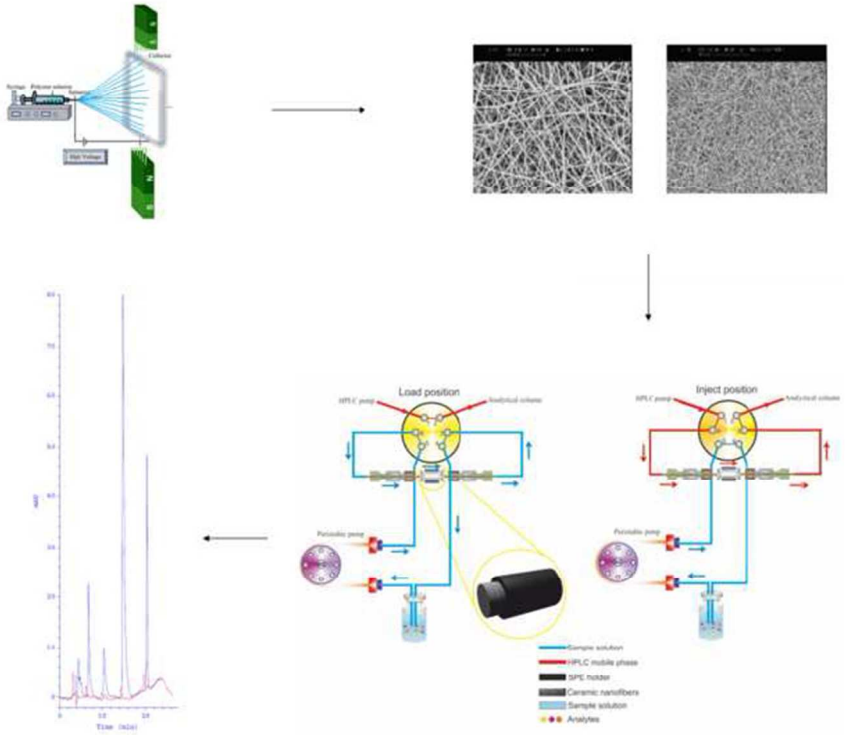

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Magnetic and electric fields assisted electrospun polyamide nanofibers for on-line *μ*-solid phase extraction and HPLC

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Abstract

The effects of applied magnetic and electric fields in electrospining were investigated to produce more efficient nanofibers. Considering the previous extensive studies, polyamide nanofibers were prepared by conventional approach and under auxiliary electric and magnetic fields. The first sorbent was synthesized by electrospinning of a solution of 18% polyamide in formic acid. The second and third types of polyamide were prepared similarly while the electrospining processes was assisted by an electric and a magnetic field, respectively. The third type of polyamide contained magnetic ionic liquid (MIL) to induce sufficient magnetic susceptibility to the polymeric solution. The SEM images revealed that the application of auxiliary electric and magnetic fields led to the aligned nanofibers with mean diameters of 200 and 90 nm, respectively while for the conventional electrospun non-woven nanofibers the mean diameter was 500 nm. To evaluate the extraction efficiency of the prepared nanofibers, they were removed from the collector electrode and packed into the μ-solid phase extraction (μ-SPE) cartridge, coupled on-line with high performance liquid chromatography (HPLC). Apart from the influence of the assisted fields on electrospining, the effects of size of the nanofibers and the ionic liquid content on the μ-SPE of imidacloprid, metribuzin, ametryn and chlorpyrifos were investigated. The highest extraction efficiency was achieved for the third sorbent due to its higher aspect ratio. After preparation of five sets of nanofibers, it was revealed that the presence of MIL dopant up to 10 % in a solution of 18% polyamide exhibited the most satisfactory results. The linearity for the analytes was in the range of

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1–500 μg L^{-1}. Limit of detection (LOD) was in the range of 0.4–4 μg L^{-1} and the RSD% values (n = 5) were all satisfactory at the 20 and 200 μg L^{-1} levels. The applicability of the developed on-line μ-SPE-HPLC method was examined by analyzing real water samples obtained from spiked Zayandeh rood river and Caspian Sea and the relative recovery percentages were from 84 to 108% at 20 and 200 μg L^{-1} levels.

Keywords: Auxiliary electrode electrospinning, magnetic field assisted electrospinning, magnetic ionic liquids, on-line μ-SPE-HPLC

1. Introduction

With the rise of worldwide trade in agricultural products in recent years, researchers are paying more attentions to the development of novel analytical techniques to monitor the pesticides residues in drinking waters. Pesticides, including insecticides, acaricides, fungicides, and herbicides usually present at trace levels throughout the whole environment. There is therefore a need to develop sensitive methods for their determination. Solid phase extraction (SPE) is a popular and well-established sample preparation method used for isolation, enrichment and/or clean-up of components of interest from aqueous samples [1]. The solid phase sorbent is usually packed into small tubes or cartridges. Recently many developments in this technology have taken place including new formats such as discs, pipette tips, 96-well plates and μ-SPE [2-5]. Preparation of new sorbents such as silica or polymer-based media and mixed- media has been also focused for several years. Synthesizing the new sorbents, however, has remained a challenging task towards preparing homogenous sorbents with improved aspect ratios.

Electrospinning is a versatile method for the production of nonwoven fibers ranging in size from nano to micro scale. Therefore, it has been adopted in various fields of science tissue engineering, energy storage, sensors and environmental engineering [6]. Electrospun nanofibers were recently applied for extraction of desired analytes by μ-SPE and solid phase microextraction [7-9]. A wide range of polymers, composites, and ceramic precursor solutions have been electrospun into non-woven fiber mats. Sometimes electrospinning is followed by secondary operations, such as heat treatment or coating the previously electrospun fibers [10]. The primary setup for electrospinning includes a spinneret with a metallic needle, a high voltage power supply, and a grounded collector. Many processing parameters affect the fiber diameter, such as distance between needle and collector, polymer flow rate, and the applied voltage. By changing the primary electrospinning set up, the construction and morphology of

the electrospun nanofibers can be altered. Electrospun fibers are randomly pointed and form nonwoven mats while for broader applications of electrospinning it is desirable to generate periodic or organized structures from nanofibers. There have been a few approaches to make well aligned nanofibers by electrospinning [11-15]. Increasing the rotational speed of the collecting drum, introducing a potential across a gap or series of gaps in the collecting electrode, introducing an external lens element or a viscous liquid environment, or rapidly oscillating a grounded frame within the liquid jet are some typical examples. All of these methods rely on minimizing the fiber instability by applying external forces on the fibers during production. Yang et al. [16] also reported an approach for fabrication of well-aligned arrays and multilayer grids by a method called magnetic electrospinning (MES). In MES, the polymer solution is magnetized by the addition of a small amount of magnetic nanoparticles. The solution is electrospun into fibers while a magnetic field generated by two parallel-positioned permanent magnets is applied. The magnetic field stretches the fibers across the gap to form a parallel array as they land on the collector. An aluminum foil collector is placed between the magnets and acts as the cathode. The length of the distance between the magnets could be changed from several millimeters to several centimeters, which determines the width of the resultant arrays.

Ionic liquids (ILs) are non-molecular solvents that have captured the interest of many in academics and are currently being introduced into a number of industrial processes worldwide [17,18]. Ionic liquids (ILs) are increasingly being used in analytical chemistry [19-22]. It has been recently used as the sorbent in microextraction techniques [23]. ILs could be easily magnetized and used as the active reagent of polymer solution for MES.

In here, the effects of electric and magnetic fields as well as the IL content on the morphology and structure of the electrospun nanofibers were investigated *via* the on-line μ-SPE-HPLC of imidacloprid, metribuzin, ametryn and chlorpyrifos. Auxiliary electrode electrospinning (AE) and

magnetic field assisted electrospinning (MFAES) led to the reduction of the nanofibers diameters. The obtained data revealed that all nanofibers have great potential for the trace enrichment purposes. The nanofibers mat prepared by MFAES was selected for further analysis and validation due to its highest extraction efficiency. While the effect of MIL was also investigated, the relative recoveries proved the ability of the prepared sorbent for analysis of the selected analytes in the river and sea samples.

2. Experimental

2.1. Instrument

A Knauer (Berlin, Germany) HPLC system including a K-1001HPLC pump, a K-1001 solvent organizer, an on-line degasser, a dynamic mixing chamber and a UV detector K2501 was used for separation and determination of analytes. The separation was performed on the MZ analytical column ODS-3 5 µm (4.6 mm × 250 mm) with MZ C18 analytical guard column (20 mm × 4.6 mm) packed with the same sorbent under ambient temperature. The solvents used as mobile phase were acetonitrile HPLC-grade and double-distillated water. The analysis was started with 60% ACN with 0.6 mL min^{-1} and after 8:30 min it was increased linearly up to 100% ACN in 4:30 min, at this time flow rate was increased to 1 mL min^{-1} and this percentage and flow rate was maintained until end of the run. The UV detection was performed at 275 nm for imidacloprid, 230 nm for metribuzin and ametryn and 280 for chlorpyrifos. A KDS100 syringe pump (KdScientific Co., Holliston, MA, US) was used for the polymer solution delivery in the electrospinning process. A Branden-burg (West Midlands, England) regulated power supply was used for electrospinning. The two permanent magnets were NdFeB, model N48 (Ningbo Strong Magnet, China) at the size of 100

x 50 x 40 millimeter (mm) and 30 x 30 x 30 mm, respectively. Their magnetic field strength were 1.4 and 0.4 tesla, respectively. The morphology and diameter of the fabricated nanofiber sheet were investigated by a TSCAN VEGA II XMU SEM Instrument (Czech Republic).

2.2. Reagents and standards

Methanol (HPLC grade), acetone, Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), manganese (II) chloride tetrahydrate and sodium hydroxide (NaOH) were purchased from Merk (Darmstadt, Germany). Nylon 6 (N6) was from Kolon industries Inc. (Korea) and formic acid prepared from Riedel-de Haën (Seelze-Hannover, Germany). Ethyl acetate, 1-Bromodecane and 1-methylimidazole also was purchased from Merk (Darmstadt, Germany). Certified standards of Imidacloprid, metribuzin, ametryn and Chlorpyrifos were supplied from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The stock solution was prepared in methanol at concentration of 1000 mg L^{-1} and stored in refrigerator at 4 °C. A work solution of standard was prepared daily by diluting this solution with doubly distilled water.

2.3. Synthesis of Ionic liquid, Decyl-3-Methylimidazolium monobromo-thrichloroferrate [DeMeIm]-[$FeCl_3Br^-$]

Equal molar amounts of 1-bromodecane and 1-methylimidazole were added into a round-bottomed flask fitted with a reflux condenser for about 24 hours at 70 °C with stirring until two phases formed. The top phase layer containing the unreacted starting materials was decanted and removed and then ethyl acetate (a volume approximately equal to half of the bottom phase) was added and followed with mixing. The ethyl acetate was then decanted and the process was repeated two more times to remove the unreacted materials. $FeCl_3.6H_2O$ was finally added (equimolar) to DeMeIm and followed by mixing to prepare the desired MIL [DeMeIm]-[$FeCl_3Br^-$] (dark brown liquid).

2.4. Preparation of electrospun nanofibers

2.4.1. Primary (unmodified) electrospinning system

The basic electrospinning system was used to prepare the conventional nanofibers. Fig. 1a shows the setup including a horizontal nozzle to Al foil collector configuration. A polymeric solution containing 18% polyamide in formic acid was loaded into the syringe and then electrosprayed by applying the DC 15 kV high voltage to two electrodes, the electrospun fibers traveled from the needle (anode) towards aluminium sheet (cathode) in a random mode to prepare the non-woven nanofibers.

2.4.2. Auxiliary electrode electrospinning

The auxiliary coiled shape electrode made of copper tube was used as the auxiliary electrode (Fig. 1b). The coil diameter was around 20 cm and distance between the needle tip and aluminum foil collector was set at 15 cm. The negative voltage was connected to the auxiliary electrode was about 5 kV. The assembled set-up was employed to prepare the second type of sorbent by electrospinning of a solution including of 18% polyamide.

2.4.3. Magnetic Field Assisted Electrospinning

As Fig.1c shows two permanent magnets were placed in parallel position of the main negative aluminum collector. A solution containing 3% of MIL doped into the 18% polyamide was used to prepare the third sorbent. The electrospinning process was also implemented under the same potential as previously used.

2.5. μ-SPE–HPLC analysis of aqueous samples

For μ-SPE device, the prepared nanofibers sheet was removed from the aluminum foil and an amount of 6 mg of sorbent was weighed and cut into small pieces to be packed in the μ-SPE cartridge. Finally μ-SPE cartridge was assembled as the HPLC loop on the six port valve for on-line extraction and preconcentration of the selected analytes. The assembled cartridge was conditioned daily prior to the first extraction by pumping the HPLC mobile phase through it to remove any contaminant and memory effect. It was used for online μ-SPE of imidacloprid, metribuzin, ametryn and chlorpyrifos, as the model analytes, from the aquatic media. Extraction was performed by passing the spiked aqueous samples through the loop. After extraction, the HPLC mobile phase was used for on-line desorption and elution of the extracted analytes from the loop to the HPLC column (Fig. 2). In all experiments, distilled water was spiked with 200 μg L^{-1} standards of analytes.

3. Results and discussion

3.1. Characteristics and efficiency of the prepared nanofibers

The surface characteristics, diameters and porosity of the prepared nanofibers were investigated by scanning electron microscopy (SEM) technique. As Fig. 3 shows all nanofibers have sufficient homogeneity and porosity while the nanofibers prepared by auxiliary AE and MFAES have more aligned structure. The presence of the pores inside the nanofibers network improved the mass transfer of the analyte throughout the nanofibers and led to the enhanced extraction efficiencies. Although all the prepared nanofibers are favorable for trace analysis but as Fig. 4 shows the MFAES-based nanofibers have dominant extraction properties.

The conventional nanofibers have non-woven structure with no regular pattern and a mean diameter of about 600 nm (Fig. 3a and 3b). Reduction in diameters of the nanofibers (about 200 nm) and therefore enhancement in their aspect ratio was achieved when the auxiliary electrode was applied

to the spray jet (Fig. 3c and 3d). Auxiliary electrode caused to increase the radical forces in contrast to the total forces toward the collector. For first and conventional nanofibers mat there was just one tensional force toward the collector which is around 1 kV cm^{-1}. In the case of second mat, electrospun under the influence of AE, there were two perpendicular forces including 1 kV cm^{-1} toward the collector (x-axis) and 0.25 kV cm^{-1} radical forces (y-axis). As a result the fibers were whipped more path rather than the conventional mat. This led to an increase in the aspect ratio for the second nanofibers mat in compared with the first one. Comparing the extraction efficiencies of these two nanofibers led to the superiority of the AE assisted nanofibers mat as well. As Fig. 3e and 3f show application of MFAES resulted in reduction of nanofibers diameters of the third nanofibers (about 100 nm) in compared with the other two nanofibers. Whipping motion is affected by the solution properties such as conductivity, surface tension, viscosity and also the external forces which can facilitated the jet stretching and result in the reducing the fibers diameters. With introducing the nanofibers in the magnetic field, the charged jet is experienced a radial Lorenz force, and the jet diameter and its direction are affected by the magnetic field gradient. As the nanofibers are spun toward the collector, they are stretched across the gap of two opposite magnetic poles along the directions right angle to the surfaces of the magnets.

As ionic liquids increase the ionic conductivity of the solution, addition of MILS cause the reduction in surface tension of polymer solution. The magnetic field can reduce fibers diameter by increasing the velocity of jet and internal alignment of fiber jet. Considering surfactant aspect, the impact of MILS on the surface tension reduction can be more dramatic. With a lower surface tension, the whipping jet is more easily stretched by the electrostatic forces, resulting in smaller fiber diameters. Additionally, fibers are more regular due to a more stable jet that encounters fewer perturbations from the surface tension effect of reducing surface area. Other effects of MILS may be reducing the solvent evaporation rate, thus extending jet stretching and reducing the fiber diameter.

3.2. Optimization

After successful preliminary results the synthesized nanofibers mat prepared by MFAES was selected for further optimization and validation. Important and influential parameters including sample flow rate through the loop, the loading time and the sample volume are needed to be optimized to achieve the best conditions. Role of MIL on the extraction efficiency was also essential to be determined. The extraction efficiencies under different experimental conditions were compared using the chromatographic peak area. Moreover, desorption time was also investigated to minimize and/or remove any possible carryover effect. Desorption process must be implemented as quickly as possible to prevent any possible peak broadening. The HPLC mobile phase composition should have sufficient strength for complete desorption of the extracted analytes, while the proper separation of the analytes in the analytical column is kept intact. Considering the selected composition of mobile phase, time duration of 3 min was chosen for prevention of any carryover. Longer desorption times were avoided to maximize the nanofibers sorbent lifetime. All optimizing parameters were performed at the concentration of 200 μg L^{-1} using the nanofibers prepared by MFAES.

3.2.1. Role of MIL

Magnetic induction of the spray in the field is attributed to the presence of MIL. The charged jet of the sprayed solution containing the doped MIL in polyamide experience a radial Lorenz force, and the jet diameter and its direction are determined by the magnetic field gradient. So, the electrospun nanofibers are more stretched and aligned with lower diameters. The presence of MIL might act as porogens and mediators for the preparation of nanofibers in which more porosity could be formed as well as direct interaction of any remaining of MIL with the target analytes. The MIL amount was

therefore investigated from 1% to 20%, and extraction efficiency was increased up to 10% of MIL (Fig. 5a). For further investigation, FTIR spectra from the conventional PA nanofibers, PA-MIL nanofibers and PA-MIL nanofibers washed with water and water/ACN were obtained. As Fig. 6 shows, the peak at 3302 cm^{-1} (NH bond) in PA nanofibers was disappeared and replaced with a broad peak for PA-MIL. This is probably due to hydrogen bonding of nitrogen in PA with MIL which consequently led to the observed peak broadening. According to the FTIR spectra, the PA-MIL nanofibers mat contained MIL even after extensive washing with water and water/ACN for several hours. Therefore, it is highly anticipated that MIL could have contributed in the extraction mechanism due to the presence of the decyl group, double bonds and π-π interactions. PA containing 10% of MIL as dopant was selected as the optimum amount for further evaluation of the method.

3.2.2. Other influential parameters

The required time to reach the extraction equilibrium is inversely proportional to the extraction flow rate. The shorter extraction time higher could be achieved at the expense of higher flow rates. In this regard, flow rates of 0.2, 0.5, 1, 2 and 3 mL min^{-1} were investigated and as expected the extraction efficiency was improved as the flow rate of the samples through the SPE cartridge was increased (Fig. 5b). More cycles are passed though the sorbents at a higher flow rate, and therefore greater detection of analytes. The higher flow rates were excluded from the investigation due to the physical limitations.

The extraction recovery strongly depends on the mass transfer of analyte from sample solution to the extracting nanofibers. The extraction time profile was studied by varying the loading time of the sample solution through the μ-SPE cartridge in the range of 5-35 min. As Fig. 5c shows the extraction efficiency was enhanced as the loading time was increased up to 25 min.

The mass of an analyte extracted by the polymeric nanofibers is related to the overall equilibrium of the analyte in the two phases. The overall equilibrium might be also dependent on/independent of the sample volume under the applied conditions. The effect of sample volume was investigated from 5 to 400 mL. As Fig. 5d shows, the extraction efficiency was nearly remained constant for all the used sample volumes and in this study it was independent of sample volume. The mass of analytes extracted by the sorbent is related to the overall equilibrium of the analytes in the two phases. Mass of the analyte extracted by the sorbent is expressed as [24]:

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \quad (1)$$

Equation (1) describes the mass extracted by the polymeric sorbent in equilibrium condition. Clearly, the number of extracted moles "n" is increased as long as sample volume V_s increased, until $K_{fs} V_f \langle\langle V_s$; then, amount of analyte extracted is independent of sample volume:

$$n = K_{fs} V_f C_0 \quad (2)$$

The effect of sample volume was investigated and varied from 5 to 400 mL. As Fig. 5d shows, the extraction efficiency is independent of sample volume. Apparently at this point the system already reached to the equilibrium and according to equation (2), increasing the sample volume has no effect on the extraction efficiency. Probably equation (1) is valid under pre-equilibrium condition which might be related to the sample volumes lower than 5 mL.

3.3. Method validation

Validation of the method was performed by determination of the target analyte based on the optimized conditions, a sampling flow rate of 3 mL min^{-1}, loading time of 25 min, desorption time of 3 min and sample volume of 5 mL. Distilled water spiked with imidacloprid, metribuzin, ametryn and chlorpyrifos was used to evaluate the precision of the measurements, LOD, LOQ, the dynamic

range and selectivity of the method. Comparison of chromatograms obtained before (direct injection of 50 μL of 200 μg L^{-1}) and after μ-SPE-HPLC of the distilled water spiked at 200 μg L^{-1} of the target analytes could be seen in Fig. 7. The linearity of the method was tested by preparing the calibration curve for analyte with 7-10 points. The linearity for the analytes was in the range of 1-500 μg L^{-1}. The regression coefficients obtained for all analytes were satisfactory ($R^2 > 0.994$). The values of LOD (S/N = 3/1) were in the range of 0.4-4 μg L^{-1} and LOQ (S/N = 10/1) 1-10 μg L^{-1}. The precision of the method was determined by performing five consecutive extractions from the aqueous solutions at two concentration levels. The standard deviations of the peak area of analyte, spiked at the concentration levels of 20 and 200 μg L^{-1}, were satisfactory (Table 1). Caspian Sea and Zayandeh rood river samples were chosen to evaluate the applicability of the developed method in real samples and to investigate the matrix effect. No peaks were observed at the desired retention times of analytes, so they were spiked at two concentration levels of 20 and 200 μg L^{-1}. The obtained results proved the robustness of the developed sorbent in real-life sample analysis (Table 2).

4. Conclusion

In this project, increasing the aspect ratio of the electrospun nanofibers due to reduction in the diameter resulted in the enhanced extraction efficiency. This was achievable by modifying the primary instrumentation of an electrospinning system via applying some external forces such as auxiliary electrode and introducing some magnets and by addition of material into a polymer solution. Addition of MIL to the solution in MFAES developed system might be helpful to induction the magnetism and also reduction the viscosity and increasing the conductivity of the polymer solution. Improving the conductivity and viscosity of the polymer solution along with surface tension and solvent evaporation rate are some of the reasons for the observed reduction in fiber diameters resulted. The PA polymer jet with higher conductivity, combined with the effect of

higher charge repulsion on jet surface due to higher concentration of charges, effectively enhance the jet stretching during whipping and further smaller diameters of the produced nanofibers. Moreover, increasing the MIL effectively improve the extraction efficiency since MIL participate on sorption process. Good extraction efficiency of the prepared sorbent along with its high solvent resistibility and reusability made it so appropriate for trace analysis of target analytes in real samples. The sorbent could be recovered frequently after each subsequent desorption.

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Figures caption

Fig. 1. Schematic diagram of three electrospinning systems. (a) Basic (unmodified) electrospinning system, (b) Auxiliary electrode electrospinning (c) Magnetic Field Assisted Electrospinning

Fig. 2. On-line μ-SPE-HPLC set-up

Fig. 3. SEM images of basic electrospinning system (a,b), AES (c,d) and MFAES (e,f) at 3 and 10 kX

Fig. 4. Comparison of the extraction efficiency of the three prepared sorbents, Distilled water was spiked with 200 μg L^{-1} of each analyte, Extraction time: 30 min, Flow rate: 3 mL min^{-1}, sample volume: 5 mL

Fig. 5. Optimization of the influential parameters on the extraction efficiency. (a) MIL percentage, (b) Sample flow rate, (c) Loading time, (d) Sample volume. Distilled water was spiked with 200 μg L^{-1} of each analyte.

Fig. 6. The IR spectra from the electrospun a) PA-MIL washed with H_2O and H_2O/ACN, b) PA-MIL c) PA

Fig. 7. Chromatograms obtained by on-line μ-SPE HPLC of the target analytes, before (direct injection) and after μ-SPE of the spiked distilled water with the analytes at concentration of 200 μg L^{-1}. Imidacloprid, metribuzin, ametryn and Chlorpyrifos are eluating respectively.

Fig. 1

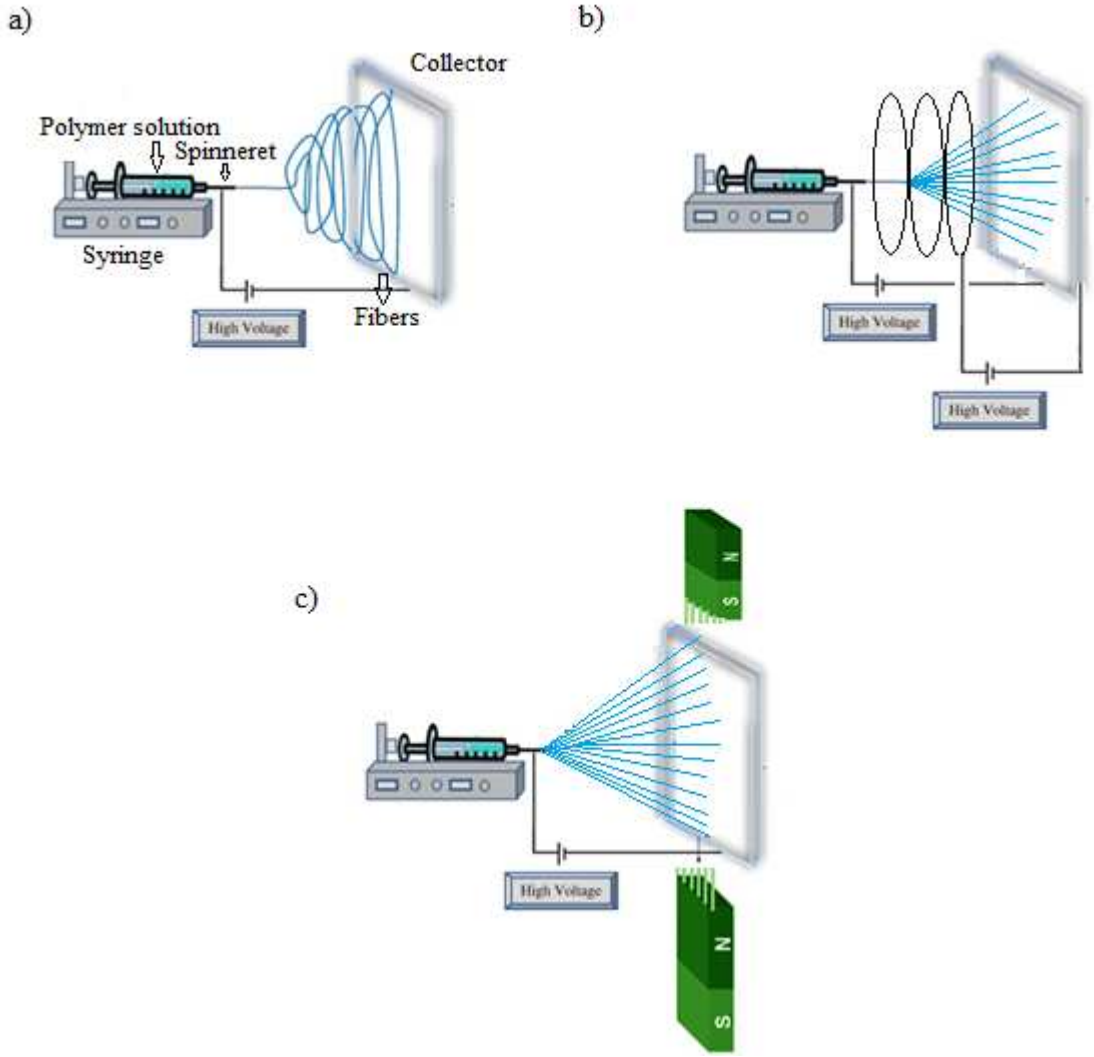

Fig. 2

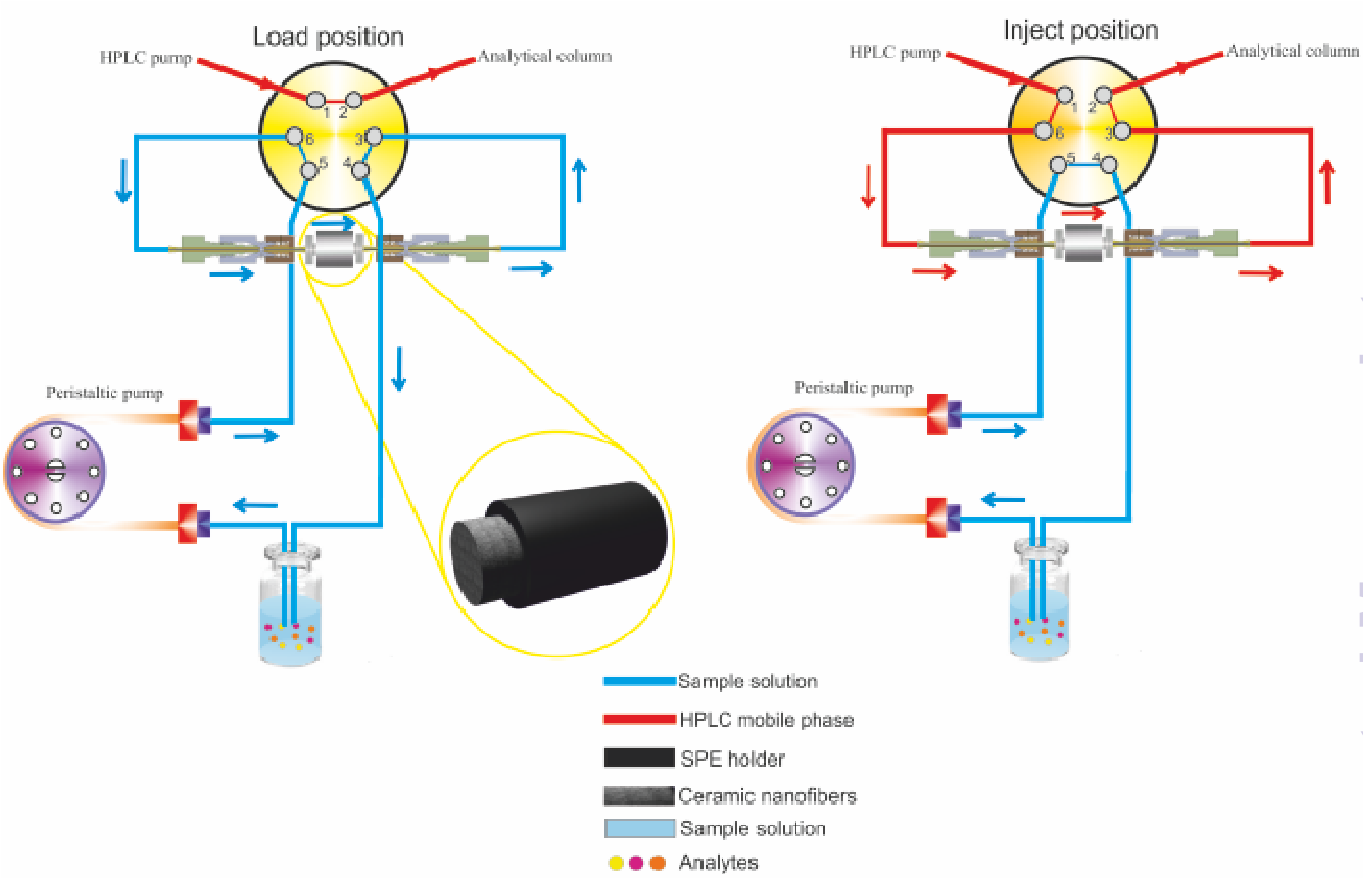

Fig. 3

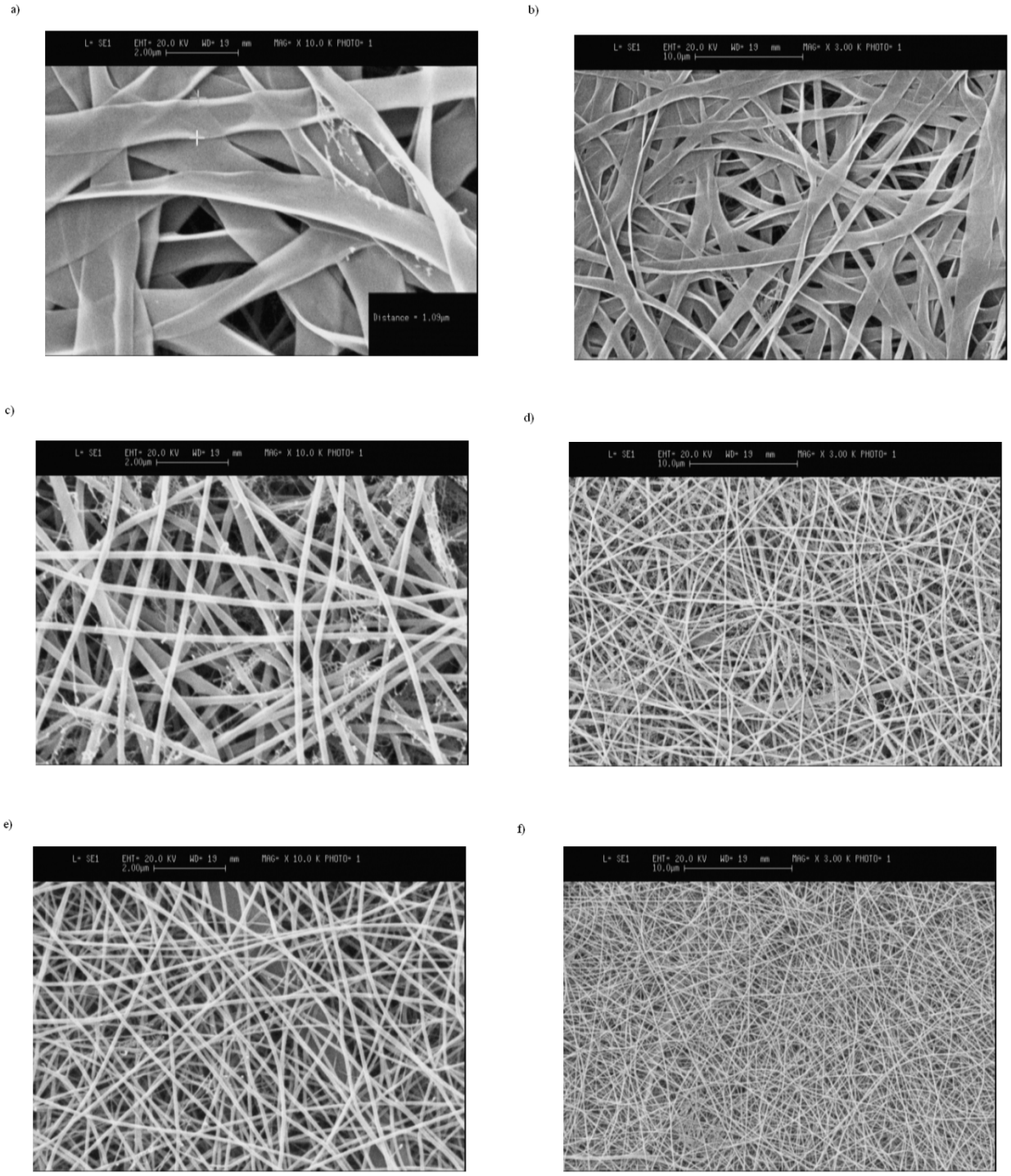

Fig. 4

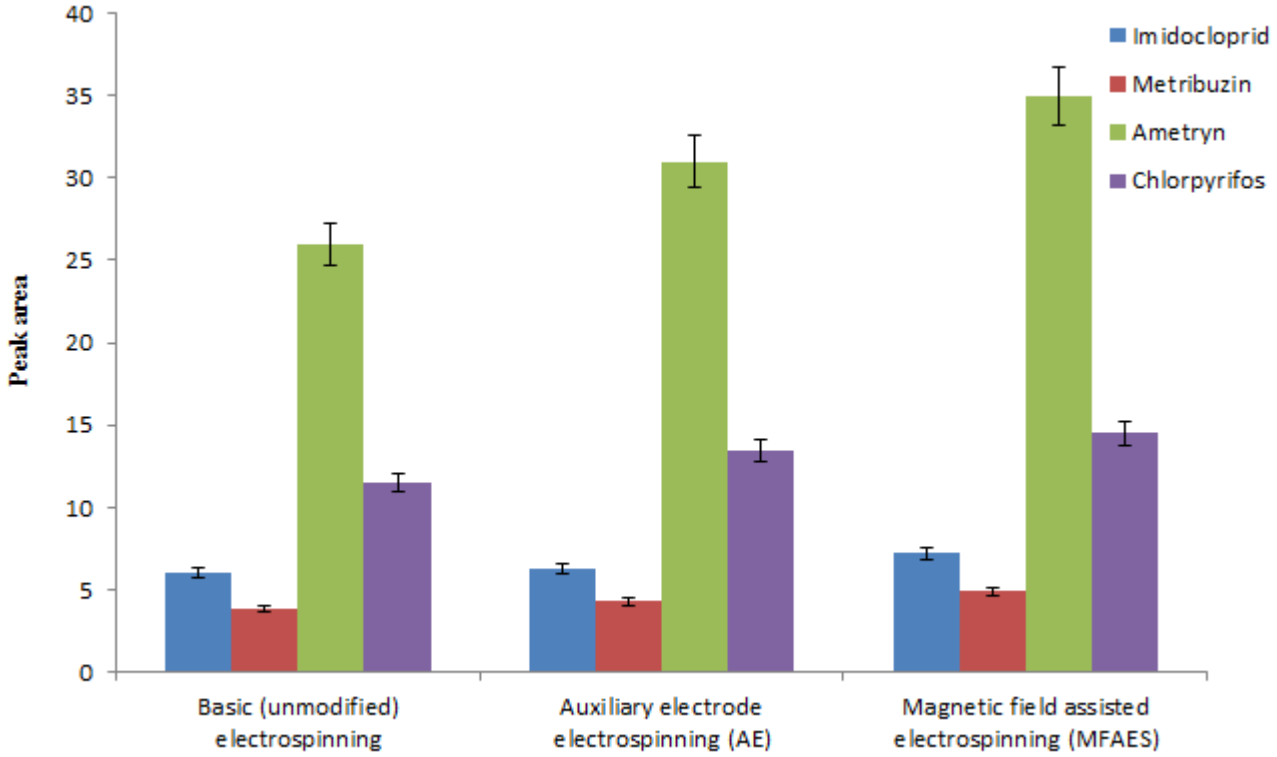

Fig. 5

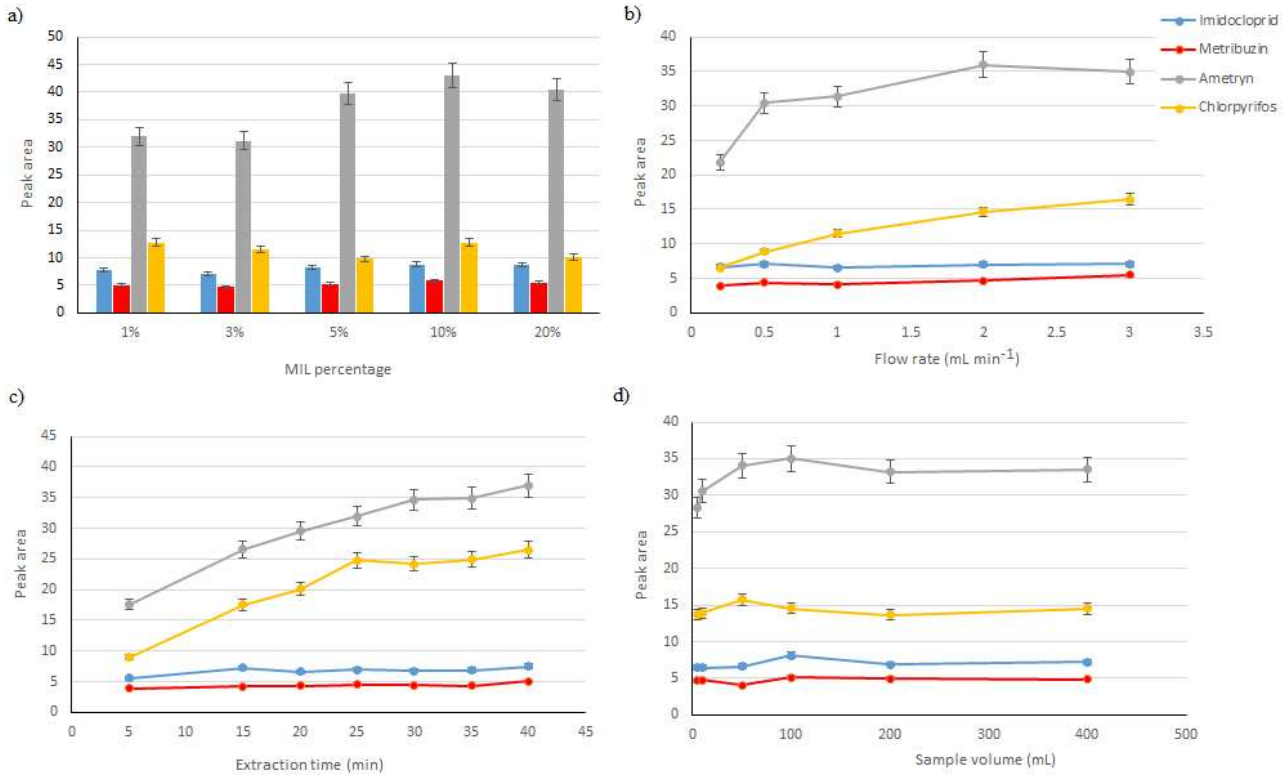

Fig. 6

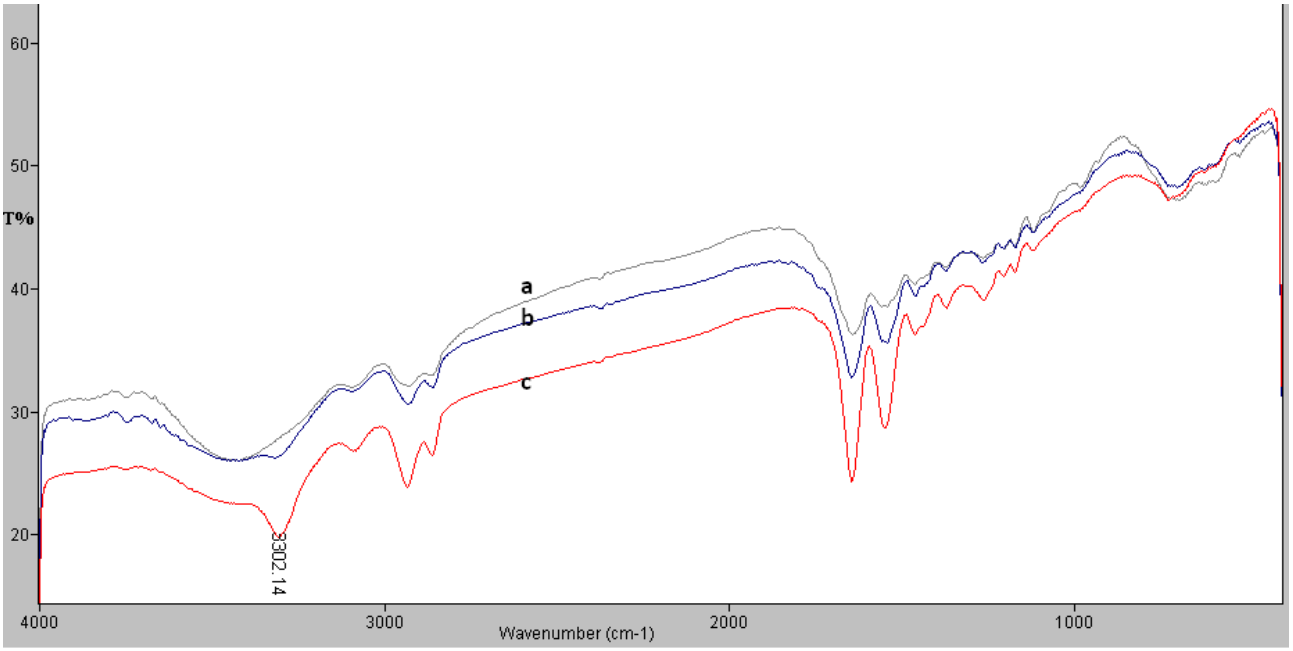

Fig. 7

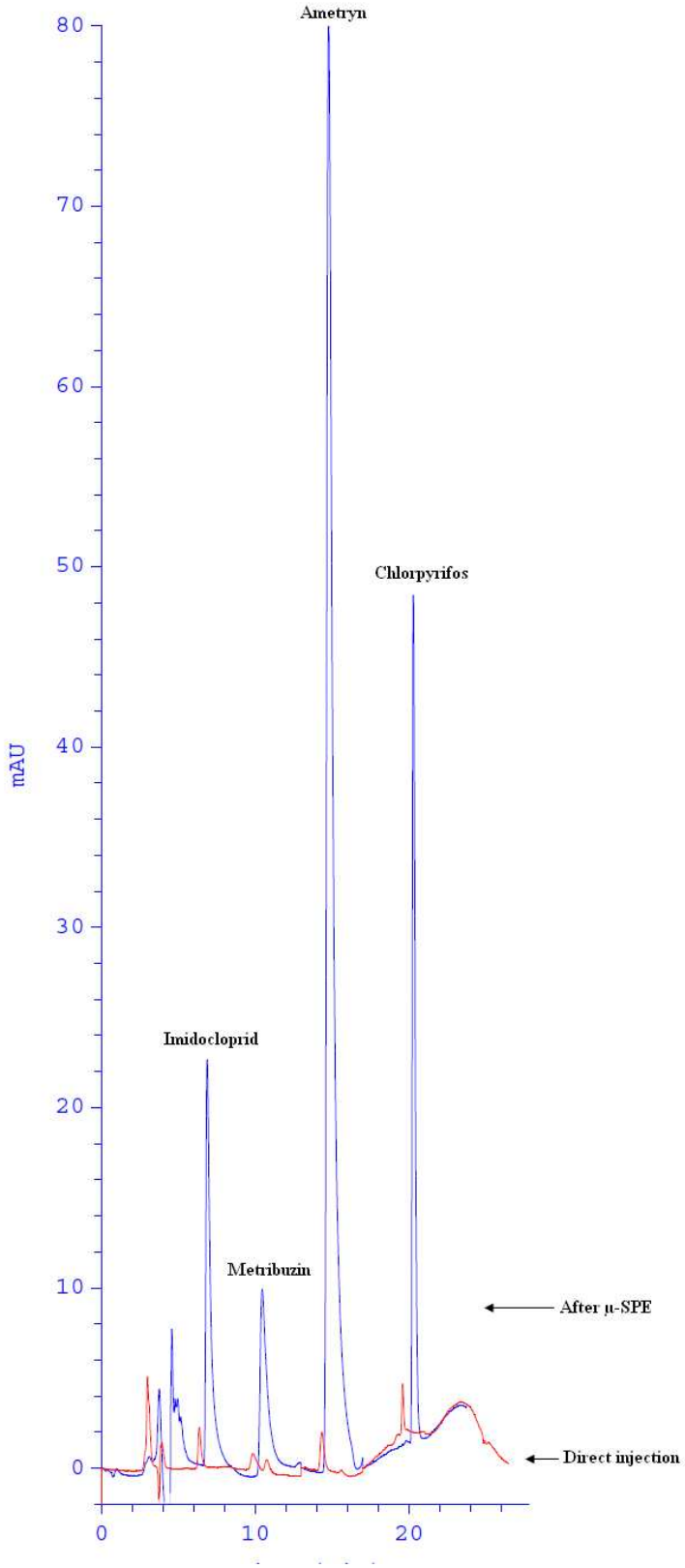

Table 1- Figures of merit of the method

Compounds	LDR[a] (µg L^{-1})	LOD [b] (µg L^{-1})	LOQ[c] (µg L^{-1})	R^2	Regression equation	RSD% (n=5)[d]	RSD% (n=5)[e]
Imidacloprid	5-500	2.0	5.0	0.9962	y = 0.0295x - 0.2856	10.5	3.8
Metribuzin	10-500	4.0	10.0	0.9941	y = 0.0185x - 0.1906	5.9	3.4
Ametryn	1-500	0.40	1.0	0.9987	y = 0.2584x + 0.63	7.3	4.8
Chlorpyrifos	3-500	1.0	3.0	0.9946	y = 0.0691x - 0.3222	11.5	3.9

[a] Linear dynamic range

[b] S/N=3

[c] S/N=10

[d] $C_{anlytes}$=20 µg L^{-1}

[e] $C_{anlytes}$=200 µg L^{-1}

Table 2

Relative recoveries for real samples spiked with the selected analytes at two concentration levels

Analyte	Zayandeh rood river				Caspian Sea			
	RR %[a]	RSD % (n=3)[*]	RR %[b]	RSD % (n=3)[b]	RR %[a]	RSD % (n=3)[a]	RR %[b]	RSD % (n=3)[b]
Imidacloprid	91	8.9	96	6.1	87	11.5	91	8.3
Metribuzin	103	8.4	95	5.4	85	9.1	93	9.1
Ametryn	108	10.3	103	5.6	104	10.4	98	8.9
Chlorpyrifos	105	10.1	92	8.8	97	11.4	107	5.5

RR: Relative Recovery

[a]$C_{analytes}$ = 20 µg L^{-1}

[b]$C_{analytes}$ = 200 µg L^{-1}