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The imprinted silica nanofibers formation via sol-gel-electrospinning intended for selective micro solid phase extraction

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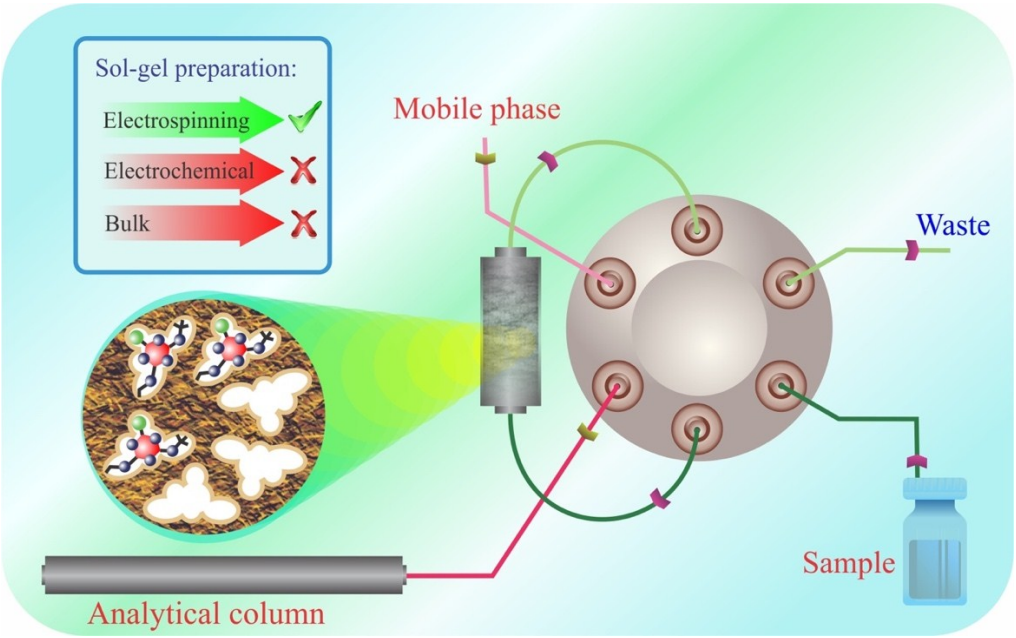

The molecular imprinted silica nanofibers were implemented toward atrazine recognition by an on–line micro–SPE–HPLC set up.

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Experimental Section

Reagents and standards

Reagents such as 3-(trimethoxysilyl)propylmethacrylate (3-TMSPM) and 3-(trimethoxysilyl)-1-propanthiol (3MPTMOS) were purchased from sigma–Aldrich (St. Louis, MO, USA). The HPLC–grade methanol and acetone along with acetonitrile and trifluoroaceticacid (TFA), sulfuric acid, copper sulfate and acetic acid were purchased from Merck (Darmstadt, Germany). Atrazine, terbutryn and ametryn were prepared from Accu-Standards (USA). Polyamide (MW 16000 g mol^{-1}) was purchased from Kolon industries Inc. (Korea). The standard stock solution of analytes was prepared in methanol-acetonitrile at concentration level of 1000 mg L^{-1} and stored in refrigerator at 4 °C. Fresh working solutions were prepared daily by diluting the stock solutions with double distilled water.

Instrumentation and chromatographic conditions

The chromatographic separation and determination was performed on a Welch Materials Inc. (Zhejiang, China) analytical column XB-C18 5 μm (4.6 mm × 250 mm) reversed phase analytical column following a Mz analytical guard column (20 mm × 4.6 mm) packed with the same material using a mobile phase flow rate of 1.0 ml min^{-1} under ambient temperature. The separation of analytes was performed using a Knauer (Berlin, Germany) HPLC system including a K-1001 HPLC pump, a K-1001 solvent organizer, an online degasser, a dynamic mixing chamber and a UV detector K2501. The HPLC pump was used to generate an isocratic elution mode and the mobile phase was acetonitrile-double distilled water (40:60, v/v) for all analytes. The maximum absorbance wavelength of triazines were determined by a 10 mg L^{-1} solution using a double beam UV-Vis spectrophotometer (Perkin- Elmer, Lambda 25) and the UV detection for HPLC was operated at 230 nm. The acidity of solution was monitored by a pH meter M 151 Martini (Italy). A magnetic stirrer (Velp Scientifica, Italy) was used for mixing the polymer solution.

The surface morphology of the silicate phase was investigated using a scanning electron microscope from VEGA 3 TESCAN SEM Instrument (Czech Republic). The SEM images were recorded after gold sputtering at the desired operating voltage.

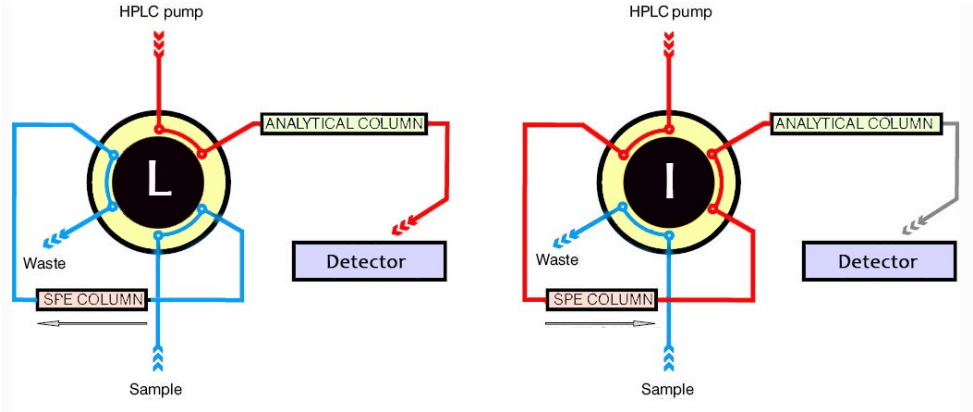
For TGA measurements, samples were tested with TGA 209 F1 Libra Netzsch Co. (Germany). The temperature was programed from 20 to 250 °C with the ramp of 10 °C min^{-1}, remained at 250 °C for 30 min and then increased to 600 °C under atmospheric pressure.

Fourier transform infrared (FT-IR) analysis was conducted on the structure of silica sol samples using ABB Bomem MB 100 spectrophotometer (Bomen, Canada).

The electrospinning solution was placed in a 1–ml syringe containing a metal needle and pumped out by a KDS100 syringe pump (Kd Scientific Co., Holliston, MA, US). A variable high-voltage power supply (West midlands, England) was used to provide 15 kV to the syringe needle tip and a metal collector, placed at a constant distance of 10 cm. The electrospun fibers were collected on a 10 × 10 cm aluminum foil while the flow rate was kept at 0.2 mL h^{-1} through the process.

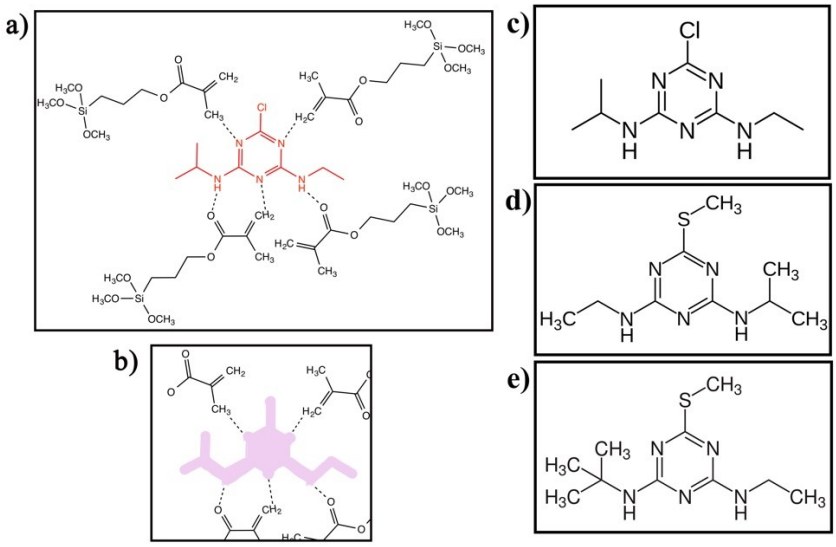
Surface area was calculated using nitrogen adsorption method at 77 K and Brunauer-Emmett-Teller (BET) analysis with an adsorpmeter (Specific Surface Area and Porosity Analyzer PHS-1020 PHSCHINA).

Fig. S1



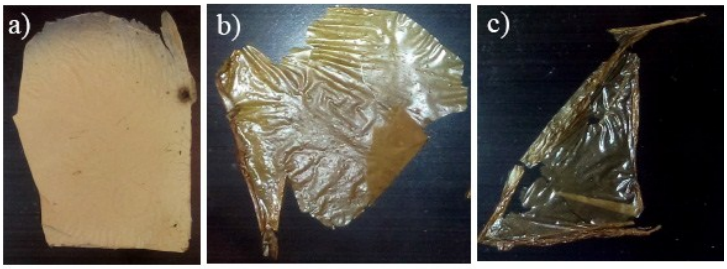
The on–line micro–SPE–HPLC set up using the ISN as the extractive phase.

Fig. S2



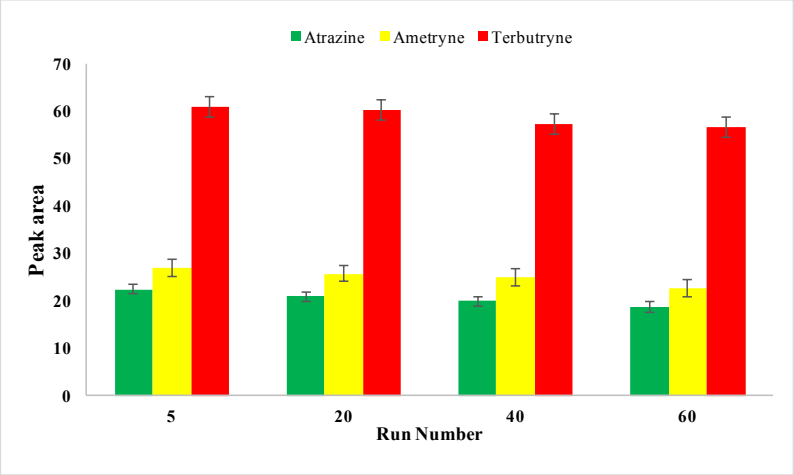
The schematic diagrams of ISN structures before (a) and after atrazine removal (b); along with molecular structures of atrazine (c), ametryn (d) and terbutryn (e).

Fig. S3



The prepared silica/PA nanofibers after electrospinning (a), 2 h heating (b), and 12 h heating (c).

Fig. S4



The peak area of atrazine, ametryn and terbutryn after more than 60 sequential extractions by ISN.