

Supplementary Information

A novel dispersive micro-solid phase extraction method combined with gas chromatography for analysis of organochlorine pesticides in aqueous samples

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Supporting Information (SI)

The following information provides a more detailed experimental describing the preparation of the nanoscale 1D-PANIs as well as specifics for the novel dispersive micro-solid phase extraction method development. Additional figures and tables are also presented to support the data described within the text.

Reagents and materials

Preparation of 1D-PANIs

1D-PANIs were prepared according to the chemical oxidation method described by Li et al. [14]. Briefly, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (0.08 M) was prepared by dissolving 4.56 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ into 250 mL HCl solution (1 M), and the aniline solution (0.32 M) was prepared by dissolving 7.45 g aniline into 250 mL HCl solution (1 M). Then, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution was poured rapidly into aniline solution. After being vigorously stirred for 30 s, the mixture was kept still for 24 h. Stirrer bars (9.5 mm in diameter \times 25mm in length) The product 1D-PANIs were collected by filtration, and washed with water/ethanol for several times and vacuum-dried at 60 °C for 8 h. The reproducibility of the synthesis of 1D-PANIs is good if we kept the experimental conditions identical.

Results and discussion

Characterisation of 1D-PANIs

The morphology of 1D-PANIs was investigated by SEM. As shown in Fig. 1s, 1D-PANIs consist of nanofibers with diameters of 30-60 nm, and the lengths of the fibers range from 100 nm up to ~1 μ m. It is worth noting that the nanofibers have agglomerated into interconnected networks. The results are well consistent with those of other studies, verifying the successful formation of 1D-PANIs [25,26].

Effect of extraction time

Owing to the high dispersity of 1D-PANIs, 10 s is enough for the 1D-PANIs to extract OCPs from water sample in a plastic dropper at 40 kHz of ultrasound frequency and 100 W of power at $25\pm 2^\circ\text{C}$. No other extraction time was needed to be investigated because no more OCPs were found to be adsorbed by 1D-PANIs after 10s.

Effect of salt addition

In general, addition of sodium chloride to an aqueous solution increases its ionic strength, which reduces the solubility of the analytes in the sample solution and improves the extraction efficiency. Therefore, the sodium chloride concentration was varied between 0 and 20% (w/v), and the effect on the extraction efficiency was observed (Fig.4s, see Supplementary Information). The results indicated that the extraction efficiencies increased as the salt concentration increased from 0 to 15% and then decreased from 15% to 20%. This is because, at the first stage, OCPs are easily transferred to the sorbent with the decrease of their solubilities in water, and at the second

stage, the increased concentration of salt ions blocks the interaction between the sorbent and OCPs, thus causing a decreased extraction efficiencies. Therefore, 15% NaCl (w/v) was chosen as the salt concentration in the following experiments.

1. Characterization of 1D-PANIs

2. Effect of sample volume on extraction efficiency

3. Effect of the amount of 1D-PANIs on the extraction efficiency

4. Effect of the salt concentration on extraction efficiency

5. Effect of the type of eluent on the extraction efficiency

6. Effect of the volume of eluent on extraction efficiency

1. Characterization of 1D-PANIs

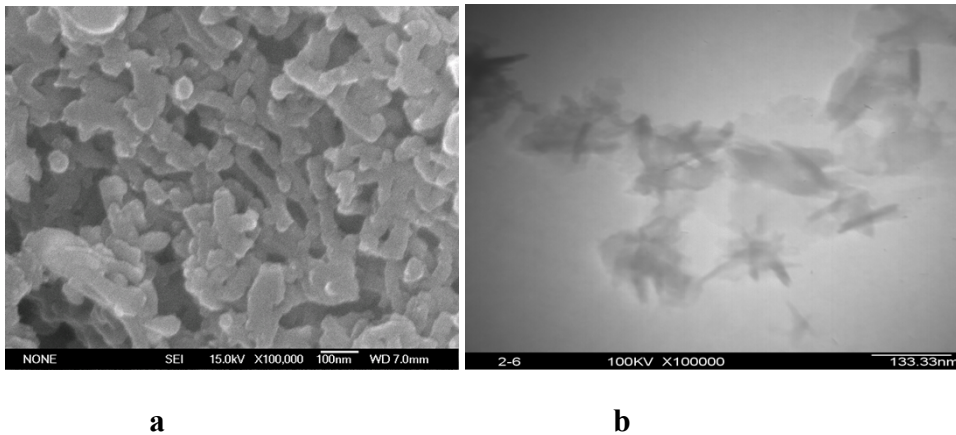


Fig. 1s (a) Scanning electron microscope (SEM) and (b) transmission electron microscope of 1D-PANIs

2. Effect of sample volume on extraction efficiency

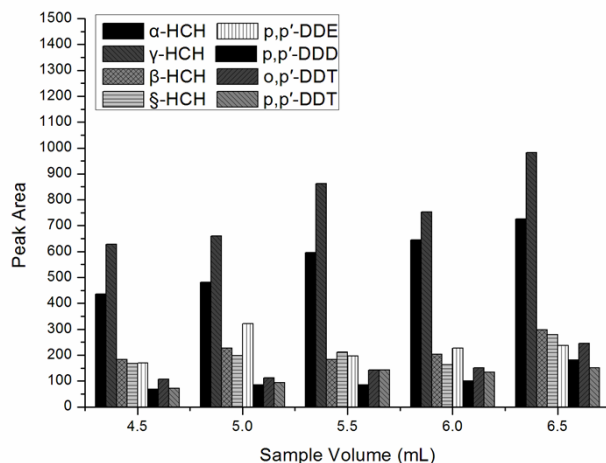


Fig.2s. Effect of sample volume on extraction efficiency. Extraction conditions: the amount of 1D-PANIs, 1 mg; eluent, n-hexane; eluent volume, 80 μ L; concentration of each OCPs, 0.5 μ g L⁻¹; ultrasound for 10 s, vibrating up and down for 30 s.

3. Effect of the amount of 1D-PANIs on the extraction efficiency.

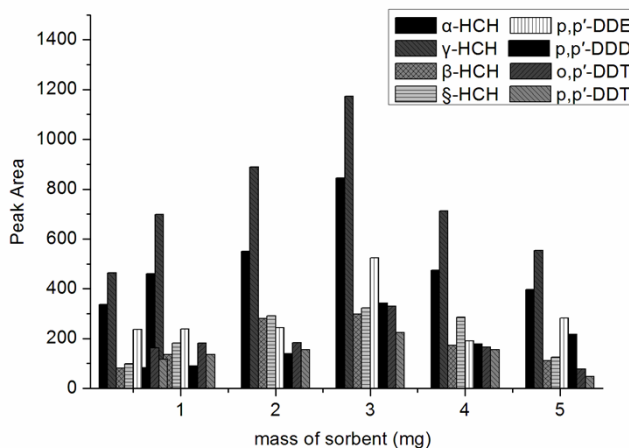


Fig.3s. Effect of the amount of 1D-PANIs on the extraction efficiency. The volume of water sample, 6.5 mL; eluent, n-hexane; eluent volume, 80 μ L; concentration of each OCPs 0.5 μ g L⁻¹; ultrasound for 10 s, vibrating up and down for 30 s.

4. Effect of the salt concentration on extraction efficiency

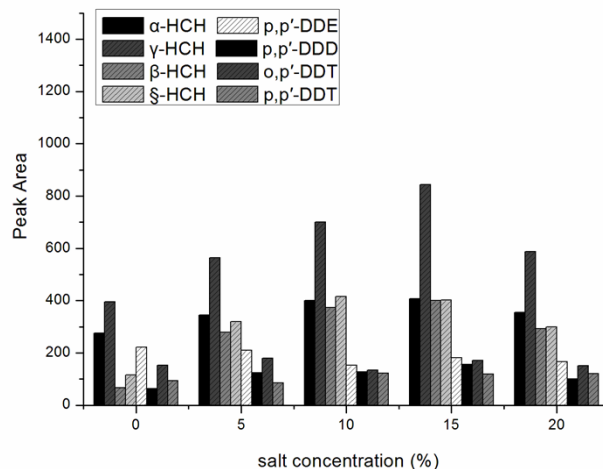


Fig.4s. Effect of the salt concentration on extraction efficiency. The volume Water sample, 6.5 mL; the amount of 1D-PANIs, 3 mg; eluent, n-hexane; the volume of eluent, 65 μL ; concentration of each OCPs $0.5 \mu\text{g L}^{-1}$; ultrasound for 10 s, vibrating up and down shaking for 30 s.

5. Effect of the type of eluent on the extraction efficiency

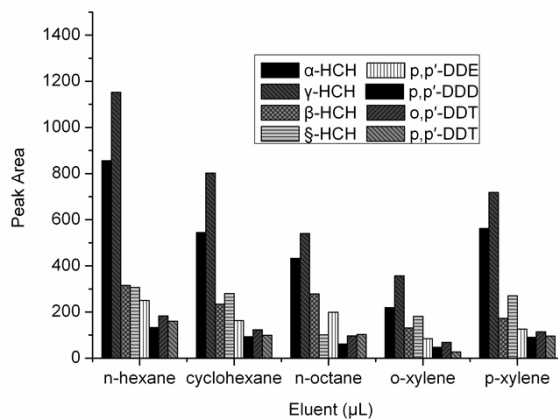


Fig.5s. Effect of the type of extractant on the extraction efficiency. The volume of water sample, 6.5 mL; the amount of 1D-PANIs, 3 mg; the volume of extractant, 80 μL ; concentration of each OCPs $0.5 \mu\text{g L}^{-1}$; ultrasound for 10 s, vibrating up and down for

30 s.

6. Effect of the volume of eluent on extraction efficiency

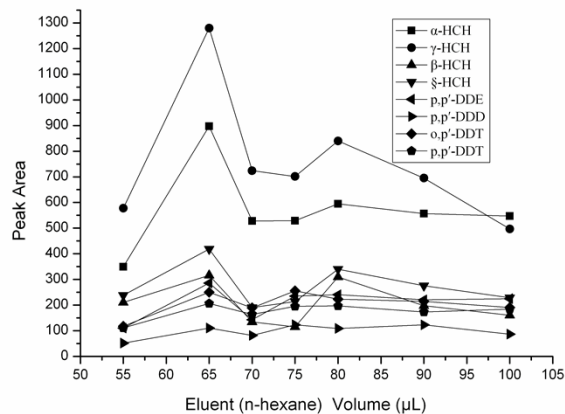


Fig.6s. Effect of the volume of eluent on extraction efficiency. The volume of water sample, 6.5 mL; the amount of 1D-PANIs, 3 mg; eluent, n-hexane; concentration of each OCPs $0.5 \mu\text{g L}^{-1}$; ultrasound for 10 s, vibrating up and down for 30 s.

References (only used in SI)

[14] D. Li, R.B. Kaner, *J. Am. Chem. Soc.*, 2006, **128**, 968-975.

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[26] J.X. Huang, S. Virji, B.H. Weiller, R.B. Kaner, *J. Am. Chem. Soc.*, 2003, **125**, 314-

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