

## ABSTRACT

A novel microextraction procedure coupled with high-performance liquid chromatography-ultraviolet detection for determination of phenoxy acidic herbicides in seawater is described. Polyvinyl chloride-polyvinyl phenol blended (PVC-PVPh) nanofiber was synthesized and used for the extraction of various phenoxy acidic herbicides from seawater. The highly porous nanofiber adsorbs the anlyate of interest with a maximum active surface area to achieve high extraction efficiency. The extraction procedure involves the stirring of 20 mL of sample solution with a PVC based PVPh nanofiber membrane (area 2x2 cm and weight about 5 mg) about 30 minutes and desorbed in a solvent by sonication. Then the solvent filtered and 20  $\mu$ L of the extract injected in High performance liquid chromatography (HPLC) and detected by Ultraviolet (UV) spectrometry. Optimum conditions for extraction and desorption were studied. The extraction efficiency was compared with conventional solid phase extraction (SPE) technique. Detection limits for Phenoxy acidic herbicides were in the range of 0.15 – 0.84 ng L<sup>-1</sup>. The sensitivity and selectivity of the polymeric nanofiber membrane could be adjusted by changing the functional group of the polymer.

## EXPERIMENTAL

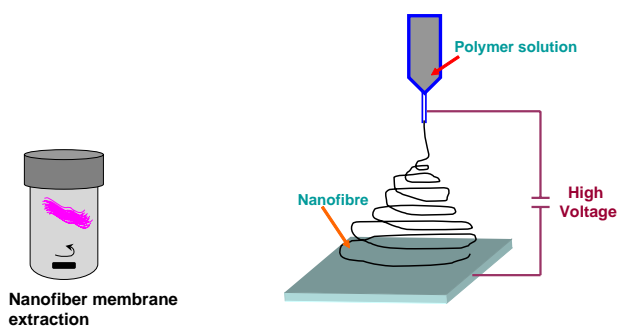


Figure. Schematic illustration of nanofiber membrane fabrication

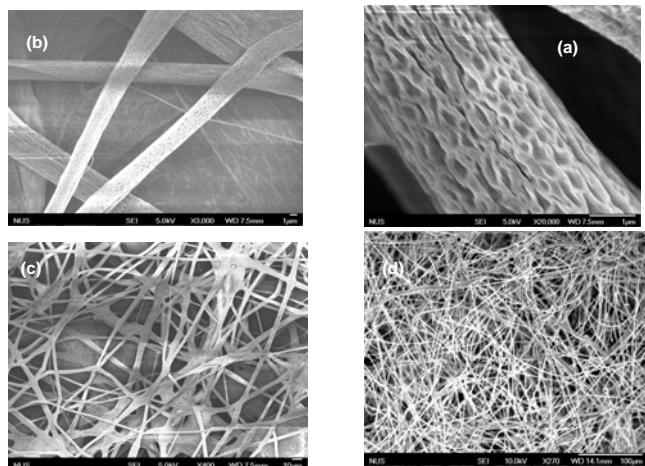
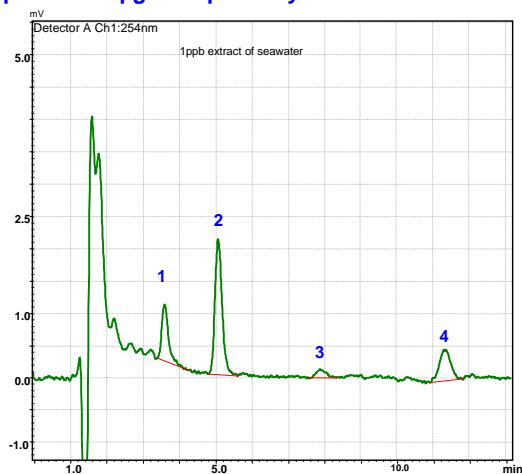


Figure. SEM images of single fiber and nanofiber membrane

Figure: HPLC-UV chromatogram of extracted seawater sample spiked at 1  $\mu$ g L<sup>-1</sup> of phenoxy herbicides



Peak identification: [1] 2,4-dichlorophenoxyacetic acid (2,4-D), [2] 2-(2,4-dichlorophenoxy) propionic acid (dicloroprop), [3] 2-(2,4,5-trichlorophenoxy)-propionic acid (Fenoprop) and [4] 4-(2,4-dichlorophenoxy) butyric acid (2,4-DB)

## CONCLUSIONS

We have successful used nanofiber membrane as a sorbent for the extraction of phenoxy herbicides from sea water coupled with HPLC-UV. This method exhibits good precision, reproducibility, and linear range response over a range of concentration. This newly developed microextraction procedure can achieve LODs in the range of 0.15 - 0.8 ng L<sup>-1</sup>. The nanofiber membrane provides a very large surface area to volume ratio with superior mechanical stiffness with tensile strength along the fiber which enhances the higher extraction efficiency. These nanofibers are compatible with established analytical techniques, such as GC and, possibly, CE, and can potentially be tailored to any class of analytes of interests by selecting suitable functional polymer for electro spinning. Unlike commercially available adsorbents, which are limited in variety, functional polymer nanofiber membrane can be designed and tailored for analyte selectivity, and synthesized in-house.

## RESULTS & DISCUSSION

Figure: Selection of suitable extraction time

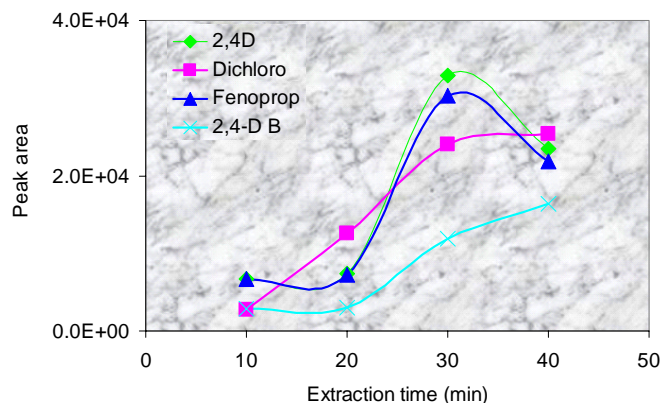
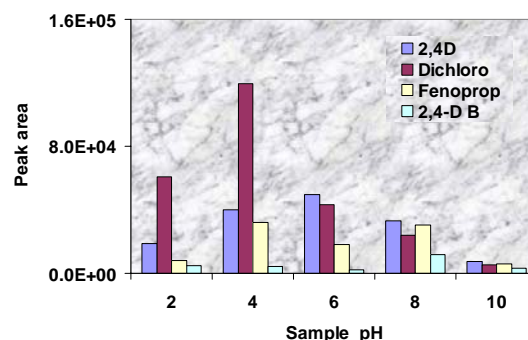


Figure: Selection of suitable sample pH



## Quantitative Analysis

Linearity range, Limits of detection and precision

Analyte	Linearity range ( $\mu$ g L <sup>-1</sup> )	R	Calibration curve	%RSD *	LOD* (ng L <sup>-1</sup> )
2,4 -D	1 -20	0.9975	y = 779.35x - 319.55	7.8	0.18
Dichloroprop	1 - 20	0.9987	y = 3248.1x + 20925	7.4	0.15
Fenoprop	1 - 20	0.9955	y = 1510.6x + 5519	4.6	0.66
2,4-D B	1 - 20	0.9977	y = 273.95x + 622.83	2.7	0.85

Recoveries of Nanofiber membrane extraction and SPE

Analyte	Nanomembrane extraction Recoveries (%)		Solid-phase extraction Recovery (%)	
	(5 $\mu$ g L <sup>-1</sup> )	(10 $\mu$ g L <sup>-1</sup> )	(5 $\mu$ g L <sup>-1</sup> )	(10 $\mu$ g L <sup>-1</sup> )
2,4-D	82.1	96.8	85.9	84.7
Dichloroprop	101.9	87.9	87.0	99.9
Fenoprop	98.2	95.0	93.7	92.9
2,4-D B	89.6	86.1	95.3	89.5